

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C09B 69/10, C08K 5/00, C09B 1/32, 1/58, 1/62, 29/033, 29/01, 29/08, 29/36, 5/14, 51/00, 31/02</p>	<p>A1</p>	<p>(11) International Publication Number: WO 98/23690 (43) International Publication Date: 4 June 1998 (04.06.98)</p>
<p>(21) International Application Number: PCT/US97/22255 (22) International Filing Date: 25 November 1997 (25.11.97) (30) Priority Data: 60/031,478 27 November 1996 (27.11.96) US 08/976,206 21 November 1997 (21.11.97) US (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventors: WEAVER, Max, Allen; 125 Hill Road, Kingsport, TN 37664 (US). KRUTAK, James, John, Sr.; 6305 Booth Court, Kingsport, TN 37663 (US). MAXWELL, Brian, Edison; 4 Shelldrake Court, Johnson City, TN 37601 (US). RHODES, Gerry, Foust; 216 Allison Court, Piney Flats, TN 37686 (US). HILBERT, Samuel, David; 210 Mulberry Lane, Jonesborough, TN 37659 (US). FLEISCHER, Jean, Carroll; 4422 Rustic Way Street, Kingsport, TN 37664 (US). PARHAM, William, Whitfield; 1807 Waters Edge Drive, Johnson City, TN 37604 (US). (74) Agent: HARDING, Karen, A.; P.O. Box 511, Kingsport, TN 37662-5075 (US).</p>	<p>(81) Designated States: BR, CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>	
<p>(54) Title: METHOD FOR PREPARING LIGHT-ABSORBING POLYMERIC COMPOSITIONS</p> <div style="text-align: center; margin: 20px 0;"> $\left[\text{A}-\text{B} \right]_n \quad (I)$ </div> <p>(57) Abstract</p> <p>The present invention recites a method comprising reacting in a solvent in the presence of a base a) at least one diacidic monomer comprising about 1 to 100 mole % of at least one light-absorbing monomer having a light absorption maximum between about 300 nm and about 1200 nm and 99-0 mole % of a non-light absorbing monomer which does not absorb significant light at wavelengths above 300 nm or has a light absorption maximum below 300 nm, with b) an organic compound of the Formula (II): X-B-X₁ wherein B is a divalent organic radical to form a light-absorbing polymeric composition having Formula (I) wherein B is as defined above; n is at least 2 and A comprises the residue of a diacidic monomer comprising about 1 to 100 mole % of at least one light-absorbing monomer having a light absorption maximum between about 300 nm and about 1000 nm and wherein the remaining portion of A comprises the residue of a non-light absorbing monomer which does not absorb significant light at wavelengths above 300 nm or has a light absorption maximum below 300 nm.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

METHOD FOR PREPARING LIGHT-ABSORBING
POLYMERIC COMPOSITIONS

5 Related Application

 This application is based upon and claims the priority of provisional application 60/031,478 filed November 27, 1996.

10 Background of the Invention

 This invention relates to an improved method for preparing light-absorbing polymeric compositions, which are useful as powders or pellets for incorporation into a variety of thermoplastic resins such as cellulose esters, polyesters, polyolefins, polycarbonates, polyamides, etc. by conventional melt or solution blending techniques. The colored thermoplastic resins thus produced have good clarity, good color development, excellent fastness to light and are useful for a variety of end uses where nonhazardous, nonmigrating, or nonextractable colorants are needed.

 It is well-known that thermoplastic polymers may be colored by adding pigments or solvent dyes (e.g., see Thomas G. Weber, Editor, *Coloring of Plastics*, John Wiley & Sons, New York, 1979). The use of pigments, however, is accompanied by undesirable properties such as opacity, dullness of color, low tintorial strength, etc. Also, difficulties in uniformly blending the insoluble pigments with the thermoplastic resin are often encountered. Also useful for coloring thermoplastic polymers are the solvent dyes (K. Venkataraman, Editor, *The Chemistry of Synthetic Dyes*, Vol. 8, Academic Press, New York, 1978, pp. 81-131), which provide compositions having improved clarity, brightness in hue and high tinctorial strength, but which may lead to dye migration, extraction, etc. from the colored thermoplastic polymer. These problems are of particular concern when solvent dyes are used to color flexible polymers such as polyvinyl chloride, polyethylene

- 2 -

and polypropylene which have low glass transition temperatures.

5 Plastics, paints, printing inks, rubber, cosmetics, and similar materials are typically colored by organic pigments when superior brilliance and tinctorial strength are important. Toxicity considerations have presented chronic problems relative to the use of organic pigments since some have been shown to be potential carcinogens and to cause contact dermatitis.

10 Plastics are also colored by using color concentrates consisting of physical admixtures of polymers and colorants (usually solvent dyes). However, the use of such physical admixtures to color polymeric materials such as polyester, e.g., poly(ethylene terephthalate) and
15 blends thereof, present a number of problems, including:

Colorant migration during drying of the colored polyester pellets.

20 Colorant migration during extrusion and colorant accumulation on dies which can cause shutdowns for clean-up. Such colorant migration and accumulation result in time consuming and difficult clean-up, particularly when a polymer of another color is subsequently processed on the same equipment.

25 Colorants may not mix well, for example, when using two or more color concentrates to obtain a particular shade.

Colorants may diffuse or exude during storage and use of the colored polymeric material.

30 The colored polymeric compositions which are prepared by the process of this invention eliminate or minimize the aforementioned problems associated with the use of conventional dyes and pigments.

Prior Art

35 To attempt to overcome some of the problems mentioned above, particularly as relates to coloring polyesters,

- 3 -

colored polyester compositions have been prepared by copolymerizing relatively low amounts of monomeric colorants during the polymer preparation (U.S. Pat. Nos. 5,194,571; 5,106,942; 5,102,980; 5,032,670; 5 4,892,922; 4,740,581; 4,403,092; 4,359,570; 4,267,306 and W092/07913). However, the preparation of these colored polymers require dyes having outstanding thermal stability since the colorants are exposed to very high temperatures for prolonged periods of time necessary for polyester 10 formation, thus severely circumscribing the selection of efficacious colorants. For example, only the nonazo type colorants have been shown to have the adequate thermal stability for copolymerization into polyesters, since azo type compounds do not have the requisite thermal stability 15 for copolymerization.

Furthermore, it is known to prepare polymeric dyes by reacting dyes containing reactive hydroxy and amino groups with organic di-acid chlorides in solvents (U.S. Pat. Nos. 2,994,693; 3,403,200; 4,619,990; 4,778,742; 5,401,612). 20 Although this method of polymer preparation allows the use of a wide range of chromophoric classes, including azo compounds, as colorant monomers, the polymerization reaction in each case involves the use of very reactive organic di-acid chlorides which are toxic and involve 25 difficult to handle inorganic halogen compounds in their preparation and have accompanying problems of hydrolysis in the presence of water which causes serious handling and storage problems. The hydrolysis product (HCl) is particularly corrosive and makes storage of these 30 compounds difficult. Furthermore, since the di-acid chlorides will react with water, the monomeric dyes must be specially dried to avoid side reactions in the polymer preparation.

In a similar attempt to prepare polymeric dyes using 35 relatively low temperatures, polyurethanes have been prepared by reacting dyes bearing two hydroxyalkyl group

- 4 -

with aliphatic and aromatic isocyanates (U.S. Pat. 5,194,463). However, the organic isocyanates themselves are extremely toxic and present difficult handling problems. They also are reactive with water and thus the
5 reaction requires specially dried monomeric dyes. Also, the colored polyurethanes as a class do not have excellent thermal stability.

It is further known to prepare colored condensation polymers by reacting a polymerizable lactone or a
10 hydroxyalkanoic acid with a dye containing reactive hydroxy group (U.S. Pat. 4,933,426). The procedure again requires relatively high reaction temperatures and prolonged times and use a large excess of the lactone reactant. The method is further hindered by the fact that
15 some lactones are suspected carcinogens.

Light-absorbing polymeric compositions have also been produced by free radical polymerization of vinyl functionalized light-absorbing monomers (U.S. Pat. Nos. 5,310,837; 5,334,710; 5,359,008; 5,434,231 and 5,461,131).

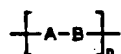
20 Finally, it is known that one may color plastics, in particular polyolefins, with low melting, cross-linked colored polyester compositions containing residues of terephthalic acid, isophthalic acid, or both, a low-molecular weight trimethylol alkane, i.e., 1,1,1-
25 trimethylol propane and a copolymerizable colorant, said colorant being present at a level of 0.1-25% by weight (U.S. Pat. No. 4,116,923). Difficulties are encountered, however, in preparing these highly cross-linked colored polymers as extreme care with regard to the temperature,
30 amount of vacuum, the level of colorant present, and the reaction time, is necessary in order to attempt to reproduce the same quality of cross-linked colored polyester composition. Further, these colored polyester compositions are brittle or low melting and may cause
35 deterioration in physical properties of thermoplastic

- 5 -

polymers when added in quantities sufficient to produce a high level of coloration.

Practice of the Invention

- 5 This invention relates to a method for preparing a light absorbing linear polymeric having Formula I



I

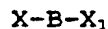
10

wherein A comprises the residue of a diacidic monomer comprising about 1 to 100 mole % of at least one light-absorbing monomer having a light absorption maximum between about 300 nm and about 1200 nm and wherein the

- 15 remaining portion of A comprises the residue of a non-light absorbing monomer which does not absorb significantly at wavelengths above 300 nm or has a light absorption maximum below 300 nm and wherein B is a divalent organic radical selected from C₂-C₁₂ alkylene, C₃-C₈ cycloalkylene, C₁-C₄ alkylene- C₃-C₈-cycloalkylene- C₁-C₄ alkylene, C₁-C₄ alkylene-arylene- C₁-C₄ alkylene, C₂-C₄ alkylene-O- C₂-C₄ alkylene, and C₂- C₄-alkylene-L-arylene- C₂-C₄ alkylene and C₂-C₄ alkylene-(L- C₂-C₄ alkylene)₁₋₄,
 20 wherein L is a linking group selected from-O-, -S-, -SO₂-, -NH-, -N(C₁-C₆ alkyl)-, -N(aryl)-, -N(SO₂ C₁-C₆ alkyl)-, -N(SO₂aryl)-, -SO₂N(C₁-C₆ alkyl)- and combinations thereof;
 25 wherein n is at least 2.

The process comprises reacting said diacidic monomer with an organic compound of Formula II

30



II

- 6 -

wherein B is as defined above and X and X₁ reactive groups and are independently selected from bromine, iodine and R-SO₂O; wherein R is selected from C₁-C₆ alkyl; C₁-C₆ alkyl substituted with chlorine, fluorine, C₁-C₆ alkoxy, aryl, aryloxy, arylthio or C₃-C₈ cycloalkyl; C₃-C₈ cycloalkyl or aryl, with said reaction being carried out in a solvent in the presence of a base; wherein the useful diacid light-absorbing monomers have Formula III

10

H-Y-H

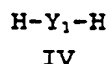
III

wherein H represents an acidic hydrogen atom; Y is a divalent light-absorbing moiety selected from a variety of chromophoric classes including azo, disazo, bis-azo, methine, arylidene, polymethine, azo-methine, azamethine, anthraquinone, anthrapyridone (3H-dibenz[f,i]isoquinoline-2,7-dione, nitroarylamines anthrapyridine (7H-dibenz[f,i]isoquinoline-7-one, phthaloylphenothiazine (14H-naphth[2,3-a]phenothiazine-8,13-dione, benzanthrone (7H (de) anthracene-7-one), anthrapyrimidine (7H-benzo[e]perimidine-7-one), anthrapyrazole, anthraisothiazole, triphenodioxazine, thiaxanthene-9-one, fluorindine (5,12-dihydroquinoxaline[2,3-b]phenazine, quinophthalone, phthalocyanine, metal phthalocyanine, naphthalocyanine, metal naphthalocyanine, nickel dithiolenes, squarylium compounds, croconium compounds, coumarin (2H-1-benzopyran-2-one), coumarin imine (2H-1-benzopyran-2-imine), perinone, benzodifuran, phthaloylacridone, phthaloylphenoxazine (14H-naphtho[2,3-a]phenoxazine-8,13-dione, phthaloylacridone (13H-naphtho[2,3-c]acridine-5,8,14-trione), anthraquinonethioxanthene (8H-naphtho[2,3-c]thioxanthene-5,8,13-trione, anthrapyridazone, pyrrolo[3,4-c]pyrrole, indigo, thioindigo, quinoline, xanthene, acridine, azine, cyanine, oxazine, 1,4 and 1,5-

- 7 -

naphthoquinones, 2,5-diarylamino-terephthalic acids and esters, pyromellitic acid diimide, naphthalene-1,4,5,8-tetracarboxylic acid diimide, 3,4,9,10-perylene-tetracarboxylic acid diimide, 3-aryl-2,5-dioxypyrroline, 5 3-aryl-5-dicyanomethylene-2-oxopyrroline, arylisoindoline, hydroxybenzophenone, benzotriazole, naphthotriazole, diminoisoindoline, naphthopyran (3H-naphtho[2,1-6]pyran-3-one and 3-imine, phthalimides, 2-arylbenzazoles, carbostyryls, 1,2-diarylethenes, 2,5-diarylthiophenes, 10 2,5-diaryl-1,3,4-oxadiazoles, triazines, 2,5-diarylfurans, 2,5-diaryl-1,3,4-thiadiazoles, thiophenes, 1,3-diphenyl-2-pyrazolines, 2-arylbenzofurans, 2,6-diphenylbenzofurans, quinolines, quinoxalines, 3,4-diarylfuranones, distyrylarenes, benzanthrones, polyarenes and 15 naphthalimides; wherein the hydrogen atoms of Formula III are independently bonded to an oxygen, sulfur, or nitrogen atom which is a part of the light absorbing moiety Y; wherein the useful non light-absorbing monomers have Formula IV,

20



wherein H represents an acidic hydrogen atom; Y₁ is a 25 divalent moiety, selected from -O₂C-R₁-CO₂- and -O-R₂-O- and -O₂C-R₃-O-, wherein R₁ is selected from C₂-C₁₂ alkylene, 1-4-cyclohexylene, arylene, arylene-O-arylene, arylene-SO₂-arylene, arylene-S-arylene, and C₁-C₄ alkylene-O-C₁-C₄ alkylene; wherein R₂ is selected from arylene, arylene-O- 30 arylene, arylene-S-arylene, arylene-SO₂-arylene, phenylene-phenylene, and phenylene-C(R₄)₂-phenylene; wherein R₄ is selected from hydrogen and C₁-C₄ alkyl; wherein R₃ is selected from arylene.

In diacid light absorbing monomers having Formula 35 III, the hydrogen atoms are preferably attached to an oxygen, a sulfur or a nitrogen atom which in combination

- 8 -

provides two acidic functional group which can produce the corresponding anions under basic conditions by removal of the protons. The acidic functional groups usually have an acid dissociation constant of about $10^{-1.5}$ to about 10^{-12}

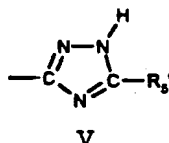
5 (pK_a of from about 1.5 to about 12). In the case of nitrogen, both protons may be attached to a single nitrogen which is attached to a sulfonyl moiety thus providing two acidic hydrogens on a single functional group.

10 Typical, acidic groups which provide one acidic hydrogen include-CO₂H, -SH, -OH attached to an aromatic ring, -CONHCO-, -SO₂-NH-CO-, -SO₂-NH-SO₂-, 1(H)-1,2,4-triazol-3-yl-, imidazolyl, benzimidazolyl, pyrazolyl, -SO₂H attached to aromatic ring, -NHSO₂R₃ and -SO₂NHR₃,
15 wherein R₃ is selected from C₁-C₆ alkyl; C₁-C₆ alkyl substituted with at least one group selected from C₁-C₆ alkoxy, aryl, aryloxy, arylthio or C₃-C₈ cycloalkyl; C₃-C₈ cycloalkyl; aryl.

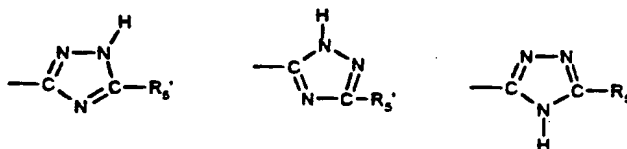
20 An example of an acidic functional group providing two acidic hydrogen attached to nitrogen is the sulfamoyl group (-SO₂NH₂).

The preferred method for producing light absorbing polymeric compositions utilizes the monomers of Formula III, wherein the protons are a part of the-CO₂H, OH
25 attached to aromatic ring, -CO-NH-CO- or 1(H)-1,2,4-triazol-3-yl functional groups. The carboxy groups are normally attached to an aromatic ring carbon or aliphatic carbon which is a part of Y. The hydroxy groups are normally attached to an unsubstituted or substituted
30 phenyl or naphthyl radical which is a part of Y. The -CO-NHCO- groups are usually attached to an aromatic ring to provide an imide such as phthalimide or naphthalimide which are a part of Y. The 1(H)-1,2,4-triazol-3-yl group has the following Formula V, wherein R₃' is

- 9 -

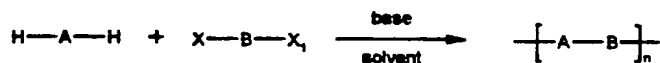


selected from hydrogen, C₁-C₆ alkyl or aryl. It should be
 5 observed that the triazole may exist in isomeric form as follows:



10 The 1(H)-1,2,4-triazol-3-yl group is preferably attached to a sulfur atom which is attached to the remainder of Y.

The method of the invention in the broadest sense involves the preparation of light absorbing polymeric compositions by reacting a diacidic monomer comprising at
 15 least 1 mole % of at least one diacidic light absorbing monomer represented by H-A-H with an organic compound containing two reactive groups represented by X-B-X₁, where B, X and X₁ are as defined above. Thus, the method
 20 may be summarized as:



The diacidic monomer H-A-H must be acidic enough to form two nucleophiles in the presence of base under
 25 convenient reaction conditions for the most advantageous process. This usually requires that diacidic monomers have pK_a values of about 12 or below.

The dinucleophilic monomer, formed by the removal of the two hydrogen atoms by the base, attacks the

- 10 -

electrophilic compound II, thus displacing anions X^- and X_1^- , with head-to-tail combination with covalent bonding to produce a linear polymer $\{-A-B\}_n$, wherein n represents the number of repeating units. The number of repeating units must be at least 2, but usually ranges between about 2 and about 25, with the preferred number being between about 3 and about 15.

Suitable bases include alkali metal carbonates; alkali metal bicarbonates; tertiary amines such as triethylamine, tri-*n*-butylamine, *N*-methylpiperidine, *N,N'*-dimethylpiperazine, *N*-methylmorpholine, *N,N,N',N'*-tetramethylethylenediamine, etc.; aromatic nitrogen bases such as pyridines, picolines, quinolines, isoquinolines, *N*-alkylpyrroles, *N*-alkylimidazoles, etc.; bicyclic nitrogen containing bases having non-hindered electron pairs, such as 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), 1,5-diazabicyclo[4,3,0]non-5-ene (DBN) and 1,4-diazadicyclo[2,2,2]octane (DABCO®).

Typical solvents useful in the polymerization reaction include aprotic polar solvents such as *N,N*-dimethylacetamide, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, *N*-methyl-*N*-phenyl formamide, dimethyl sulfoxide, aliphatic nitriles, sulfolane, hexamethyl phosphoramide, etc. and mixtures thereof. Water, alcohols, ketones pyridine and ether-alcohols, such as the Cellosolves, also are sometimes useful. One requirement is that the solvent not form a stronger nucleophile in the presence of the base than that obtained from the diacidic monomer H-A-H.

The new improved process of the invention allows the preparation of near ultraviolet (UV-A, UV-B and UV-C), visible and near infrared light absorbing linear polymeric compositions at relatively low temperatures, usually at from about 75°C to about 125°C, without prolonged heating times. Furthermore, the method is adaptable to batch-process production which is advantageous for expensive

- 11 -

products such as colorants, near infrared absorbers and near ultraviolet absorbers. The method is adaptable to a wide range of chromophoric classes since the polymer preparative reaction is carried out at relatively low temperature, which for example, allows colored polymeric compositions to be readily prepared from the very important azo class of colorants.

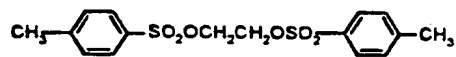
The preferred reactants of Formula II

10 $X-B-X_1$

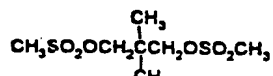
are the disulfonate compounds where X and X_1 are both a sulfonate ester of the formula-OSO₂R, wherein R is selected from C₁-C₄ alkyl, phenyl or p-methylphenyl and wherein B is selected from C₂-C₆ alkylene, -CH₂-1,4-cyclohexylene-CH₂-, 2,2,4,4-tetramethyl-1,3-cyclobutylene, 1,4-cyclohexylene, -CH₂CH₂(OCH₂CH₂)₂₋₃ and -CH₂CH₂O-1,4-phenylene-O-CH₂CH₂-. Particularly, preferred reactants of Formula II are those where B is selected from -CH₂CH₂-, -CH₂CH(CH₃)CH₂-, -CH₂C(CH₃)₂CH₂-, -(CH₂)₄-, -(CH₂)₆-, -CH₂CH₂(OCH₂CH₂)₂₋₄ and -CH₂-1,4-cyclohexylene-CH₂-.


Typical reactants of Formula II are as follows:

CH₃SO₂OCH₂CH₂OSO₂CH₃
1,2-Ethanediol,
dimethanesulfonate


1,2-Ethanediol,
bis(4-methylbenzenesulfonate)

CH₃SO₂O(CH₂)₆OSO₂CH₃
1,6-Hexanediol,
dimethanesulfonate


1,3-Propanediol,2,2-dimethyl-,
dimethanesulfonate

CH₃SO₂OCH₂--CH₂OSO₂CH₃
1,4-Cyclohexanedimethanol,
dimethanesulfonate

CH₃SO₂OCH₂CH₂OCH₂CH₂OSO₂CH₃
Ethanol,2,2'-oxybis-,
dimethanesulfonate

- 12 -

The invention also relates to a light absorbing linear polymeric composition having Formula Ia:



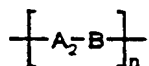
5

Ia

wherein A_1 comprises the residue of at least one diacidic monomer having a light absorption maximum between about
 10 300 nm and about 1200 nm, preferably between about 325 nm and 1100 nm and most preferably between about 350 nm and 1000 nm and wherein B is defined above and which has been prepared by reacting a diacid light-absorbing monomer of
 15 Formula III (H-Y-H) as defined above with an organic compound having Formula II (X-B- X_1) as defined above, with the polymer producing reaction having been carried out in a solvent in the presence of base.

The invention also relates to a light absorbing linear polymeric composition having Formula Ib

20



Ib

wherein A_2 comprises the residue of at least one diacidic
 25 monomer, having a light absorption maximum between about 300 nm and about 1200 nm, preferably between about 325 nm and 1100 nm and most preferably between about 350 nm and 1000 nm and which comprises at least about 50% by weight of the total of the composition of Formula Ib and wherein
 30 the remainder of A_2 comprises the residue of at least one non-light absorbing monomer of Formula IV above, and

- 13 -

wherein said polymeric composition has been prepared by reacting diacidic monomers of Formula III and Formula IV with an organic compound having Formula II above, with the polymer producing reaction having been carried out in a solvent in the presence of base.

The polymer compositions of Formula I, Ia, and Ib are referred to as "polydyes" herein when they absorb visible light thus rendering them strongly colored.

The invention further relates to a thermoplastic polymeric composition which comprises a thermoplastic polymer blended with at least one light absorbing linear polymeric composition of Formula I, Ia or Ib above. The thermoplastic polymeric composition is usually selected from polyesters, polyolefins, polyamides, polyimides, polyvinyl chloride, polyurethanes, polycarbonates, cellulose esters, polyacrylates, polyvinylesters, polyester-amides, polystyrene, polyacrylonitrile-butadiene-styrene and polystyrene-acrylonitrile. The preferred thermoplastic polymeric composition comprises the light-absorbing polymeric compositions of Formula Ia.

The invention also relates to some of the diacidic light absorbing monomers used to prepare the light absorbing polymeric composition of Formula I, Ia, or Ib.

Preferred azo compounds useful in the practice of the invention correspond to Formula VI



VI

wherein R_6 is the residue of an aromatic or heteroaromatic amine which has been diazotized and coupled with a coupling component H-Z and is preferably derived from the

- 14 -

- aromatic and heteroaromatic amine classes of aniline, 1-aminonaphthalene, 1-aminoanthraquinone, 4-aminoazobenzene, 2-aminothiazole, 2-aminobenzothiazole, 3-amino-2,1-benzisothiazole, 2-aminothieno[2,3-d]thiazole,
- 5 5-aminoisothiazole, 5-aminopyrazole, 4-aminopyrazoloisothiazole, 2-amino-1,3,4-thiadiazole, 5-amino-1,2,4-thiadiazole, 5-amino-1,2,3-triazole, 2-amino-1,3,4-triazole, 2(5) aminoimidazole, 3-aminopyridine, 2(3) aminothiophene, 2(3) aminobenzo[b]thiophene, 2-
- 10 aminothieno[3,2-b]thiophene, 3-aminothieno[2,3-c]isothiazole, 3-amino-7-benz-2,1-isothiazole, 3-aminobenzothienoisothiazole, 3-aminoisothiazole[3,4-d]pyrimidine, 5-amino-1,2,3-triazole, 3(4) aminophthalimide and 5(6) amino-1,2-benzisothiazolon-1,1-dioxide with said aromatic and heteroaromatic ring systems being unsubstituted or substituted with one or more groups selected from C₁-C₁₀ alkyl, C₁-C₆ alkoxy, C₃-C₆ cycloalkyl, carboxy, halogen, C₁-C₆ alkoxycarbonyl, formyl, C₁-C₆ alkanoyl, C₁-C₆ alkanoyloxy, dicyanovinyl, C₃-
- 20 C₈-cycloalkanoyl, thiocyano, trifluoroacetyl, cyano, carbamoyl, -CONH C₁-C₆ alkyl, CONHaryl, CON(C₁-C₆ alkyl)₂, sulfamoyl, SO₂NH C₁-C₆ alkyl, SO₂N(C₁-C₆ alkyl)₂, SO₂NHaryl, SO₂NH C₃-C₈ cycloalkyl, CONH C₃-C₈ cycloalkyl, aryl, aroyl, -NHSO₂ C₁-C₆ alkyl, -N(C₁-C₆ alkyl)SO₂ C₁-C₆ alkyl, -NHSO₂
- 25 aryl, NHCO C₁-C₆ alkyl, NHCO C₃-C₈ cycloalkyl, NHCOaryl, NHCO₂ C₁-C₆ alkyl, NHCONH C₁-C₆ alkyl, NHCONHaryl, N(C₁-C₆ alkyl)aryl, arylazo, heteroaryl, aryloxy, arylthio, C₃-C₈ cycloalkoxy, heteroarylazo, heteroarylthio, arylsulfonyl, tricyanovinyl, aryloxysulfonyl, C₁-C₆ alkylsulfonyl,
- 30 trifluoromethyl, fluorosulfonyl, trifluoromethylsulfonyl, thiocyano, hydroxy, nitro or CH=D, wherein D is the residue of an active methylene compound as defined below.

Z is the residue of an electron rich coupling component selected from the classes of anilines, 1-

35 aminonaphthalenes, 1,2-dihydroquinolines, 1,2,3,4-tetrahydroquinolines, benzmorpholines (3,4-dihydro-2H-

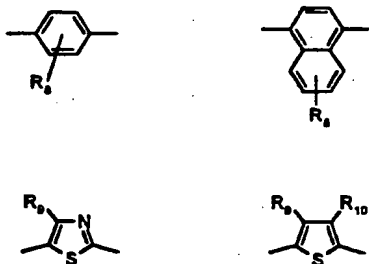
- 15 -

1,4-benzoxazine), pyrazolones, pyrazoles, 3-cyano-6-hydroxy-2-pyridones, 2,3-dihydroindoles, indoles, 4-hydroxycoumarins, 4-hydroxy-2-quinolones, imidazo[2,1-b]thiazoles, julolidines (2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizines), 1-oxajulolidines, 1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolines, 2,6-diamino-3-cyanopyridines, 2-aminothiazoles, 2-aminothiophenes, 5,5-dimethyl-1,3-cyclohexanedione (dimedone), phenols, naphthols, 2,4-pentanediones or acetoacetarilides; with
 10 the proviso that the compounds of Formula VI contain two acidic functional groups containing one acidic hydrogen each or contain one sulfamoyl group ($-\text{SO}_2\text{NH}_2$) which contains two acidic hydrogens.

Preferred disazo compounds correspond to Formula VII

15 $\text{R}_6-\text{N}=\text{N}-\text{R}_7-\text{N}=\text{N}-\text{Z}$ VII

wherein R_6 and Z are as defined above and R_7 is a divalent aromatic or heteroaromatic radical selected from the classes 1,4-phenylene, naphthalene-1,4-diyl, thiazol-2,5-diyl and thiophene-2,5-diyl:
 20

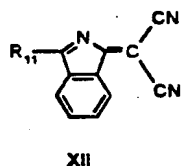
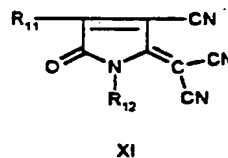
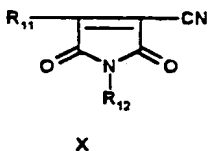
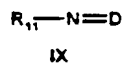
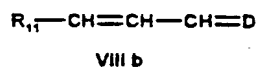
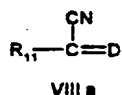
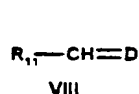


25 wherein R_6 is selected from hydrogen or 1-2 groups selected from C_1-C_6 alkyl, C_1-C_6 alkoxy, cyano, halogen, $-\text{NHCO}$ C_1-C_6 alkyl, $-\text{NHCO}_2$ C_1-C_6 alkyl, $-\text{NHCO}$ aryl, $-\text{NHCONH}$ aryl or NHCONH C_1-C_6 alkyl; R_9 is selected from hydrogen, C_1-C_6 alkyl, halogen, aryl, heteroaryl; R_{10} is selected from hydrogen, C_1-C_6 alkoxycarbonyl, cyano, carbamoyl,

- 16 -

aryl, arylsulfonyl, aroyl, -CONH C₁-C₆ alkyl, or C₁-C₆ alkylsulfonyl; with the provision that two acidic functional groups containing one acidic hydrogen each or one functional group containing two acidic hydrogens are present on compounds of Formula VII.

The preferred methine, arylidene, polymethine, azamethine, 3-aryl-2,5-dioxypyrroline, 3-aryl-5-dicyanomethylene-2-oxopyrroline and aryl isoindoline compounds correspond to Formula VIII, VIIIa, VIIIb, IX, X, XI and XII, respectively:



wherein R₁₁ is the residue of an aniline, 1-naphthylamine, 1,2-dihydroquinoline, 1,2,3,4-tetrahydroquinoline, 1,3,3-trimethyl-2-methyleneindole, 1,3-dihydro-2-methylene-1,1,3-trimethyl-2H-benz[e]indole, imidazo [2,1-b] thiazole, benzomorpholine (3,4-dihydro-2H-1,4,benzoxazine), indole, 2,3-dihydroindole, 2-aminothiazole, julolidine (2,3,6,7-tetrahydro-1H, 5H- benz [ij] quinolizine, 1-oxajulolidine, 4H-pyrrolo [3,2,1-ij]-quinoline, phenol, naphthol, thiophenol, pyrrole,

- 17 -

pyrazole, furan, thiophene, carbazole, phenothiazine or phenoxazine compound; R_{12} is selected from hydrogen, C_1 - C_{10} alkyl, C_3 - C_8 alkenyl, C_3 - C_8 -alkynyl, C_3 - C_8 cycloalkyl, aryl, $-(CH_2CH_2O)_{1-3}$ R_{13} and C_1 - C_4 alkylene- C_3 - C_8

- 5 cycloalkylene, wherein the C_1 - C_6 alkyl groups may be substituted by at least one group selected from carboxy, C_1 - C_6 carbalkoxy, C_1 - C_6 alkanoyloxy, cyano, hydroxy, chlorine, fluorine, C_1 - C_6 alkoxy, C_3 - C_8 cycloalkyl or aryl; R_{13} is selected from hydrogen, C_1 - C_6 alkoxy or C_1 - C_6
- 10 alkanoyloxy; wherein D is the residue of an active methylene compound selected from malononitrile, α -cyanoacetic acid esters, malonic acid esters, α -cyanacetic acid amides, α - C_1 - C_6 alkylsulfonylacetonitriles, α -arylsulfonylacetonitriles, α - C_1 - C_6 alkanoylacetonitriles,
- 15 α -aroylacetonitriles, α -heteroarylacetonitriles, bis(heteroaryl)methanes, 1,3-indanediones, 2-furanones, benzo-2-furanones, naphtho-2-furanones, 2-indolones, 3-cyano-1,6-dihydro-4-methyl-2,6-dioxy (2H)-pyridines, benzo
- 20 (b) thieno-3-ylidene propane dinitrile-5,5-dioxides, 1,3-bis (dicyanomethylene) indanes, barbituric acid, 5-pyrazolones, dimedone, 3-oxo-2,3-dihydro-1-benzothiophene-1,1-dioxides or aryl- $C(CH_3)C=C(CN)_2$, with the proviso that two acidic functional groups containing one acidic
- 25 hydrogens are present in compounds of Formula VIII, VIIIA, VIIIB, IX, X, XI, and XII.

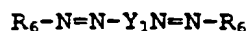
Preferred azo-methine compounds correspond to Formula XIII



wherein D, R_7 , and Z are as defined previously.

The bis-azo compound corresponds to Formula VIIa

35



- 18 -

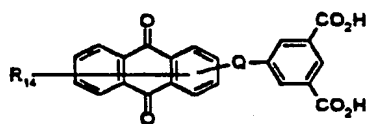
VIIa

wherein R_6 is as defined above and Y_1 is the residue of a bis coupling component selected from the classes of
5 anilines, 1,2-dihydroquinolines, 1,2,3,4-tetrahydroquinolines, benzomorpholines (3,4-dihydro-2H-1,4-benzoxazines), 3-cyano-6-hydroxy-2-pyridones, 2,6-diaminopyridines, 2,3-dihydroindoles, naphthylamines, 2-aminothiazoles, or a combination of these; with the
10 provision the compounds of Formula VIIa contain two acidic functional groups containing one acidic hydrogen each or contain one sulfamoyl group ($-SO_2NH_2$) which contains two acidic hydrogens.

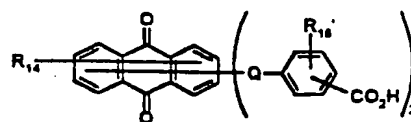
Several diacid monomers which are described in U.S.
15 Patent Nos. 4,804,719 and 3,689,501 are useful in the practice of the invention, including various anthraquinones, anthrapyridones, anthraisothiazoles, anthraprimidines, anthraprimidones, phthaloylacridones, etc.

20 Some of the preferred anthraquinone, anthrapyridone and anthraprimidine compounds correspond to the light absorbing compounds of Formulae XIV- XIXf

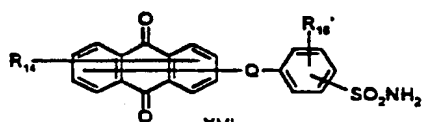
- 19 -



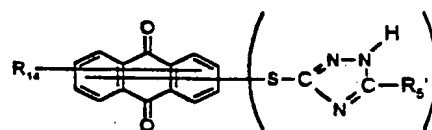
XIV



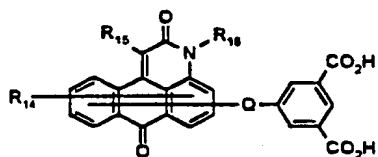
XV



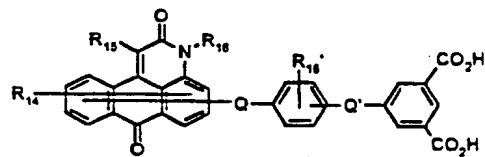
XVI



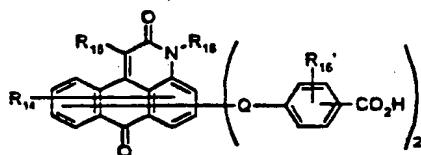
XVII



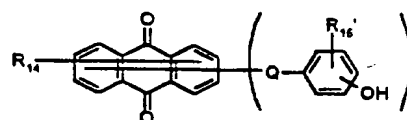
XVIII



XVIII a

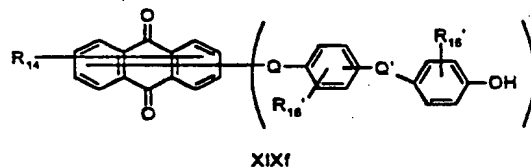
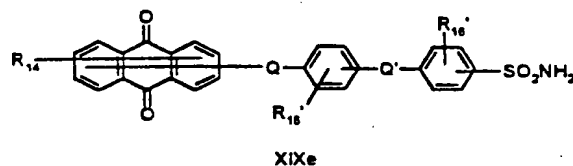
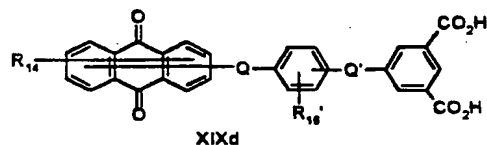
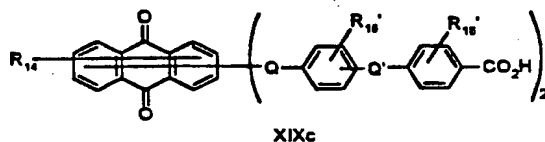
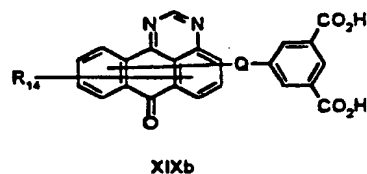
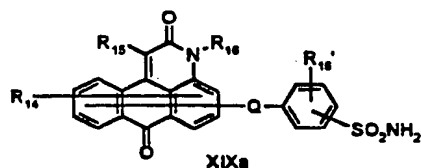


XVIII b



XIX

- 20 -

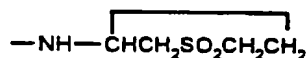


wherein R_{14} is selected from the group consisting of hydrogen, 1-4 groups selected from amino, C_1 - C_{10}

- 5 alkylamino, C_3 - C_8 alkenylamino, C_3 - C_8 alkynylamino, C_3 - C_8 cycloalkylamino, arylamino, halogen, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, aryl, aroyl, C_1 - C_6 alkanoyl, C_1 - C_6 alkanoyloxy, NHCO C_1 - C_6 alkyl, NHCOaryl, $NHCO_2$ C_1 - C_6 alkyl, $NHSO_2$ C_1 - C_6 alkyl, $NHSO_2$ aryl, C_1 - C_6 alkoxy carbonyl, aryloxy, arylthio,
- 10 heteroarylthio, cyano, nitro, trifluoromethyl, thiocyno, SO_2C_1 - C_6 alkyl, SO_2 aryl, $-SO_2NH$ C_1 - C_6 alkyl, $-SO_2N(C_1$ - C_6 alkyl) $_2$, $-SO_2N(C_1$ - C_6 alkyl) aryl, CONH C_1 - C_6 alkyl, $CON(C_1$ - C_6 alkyl) $_2$, $CON(C_1$ - C_6 alkyl) aryl, C_1 - C_6 alkyl, furfurylamino,

- 21 -

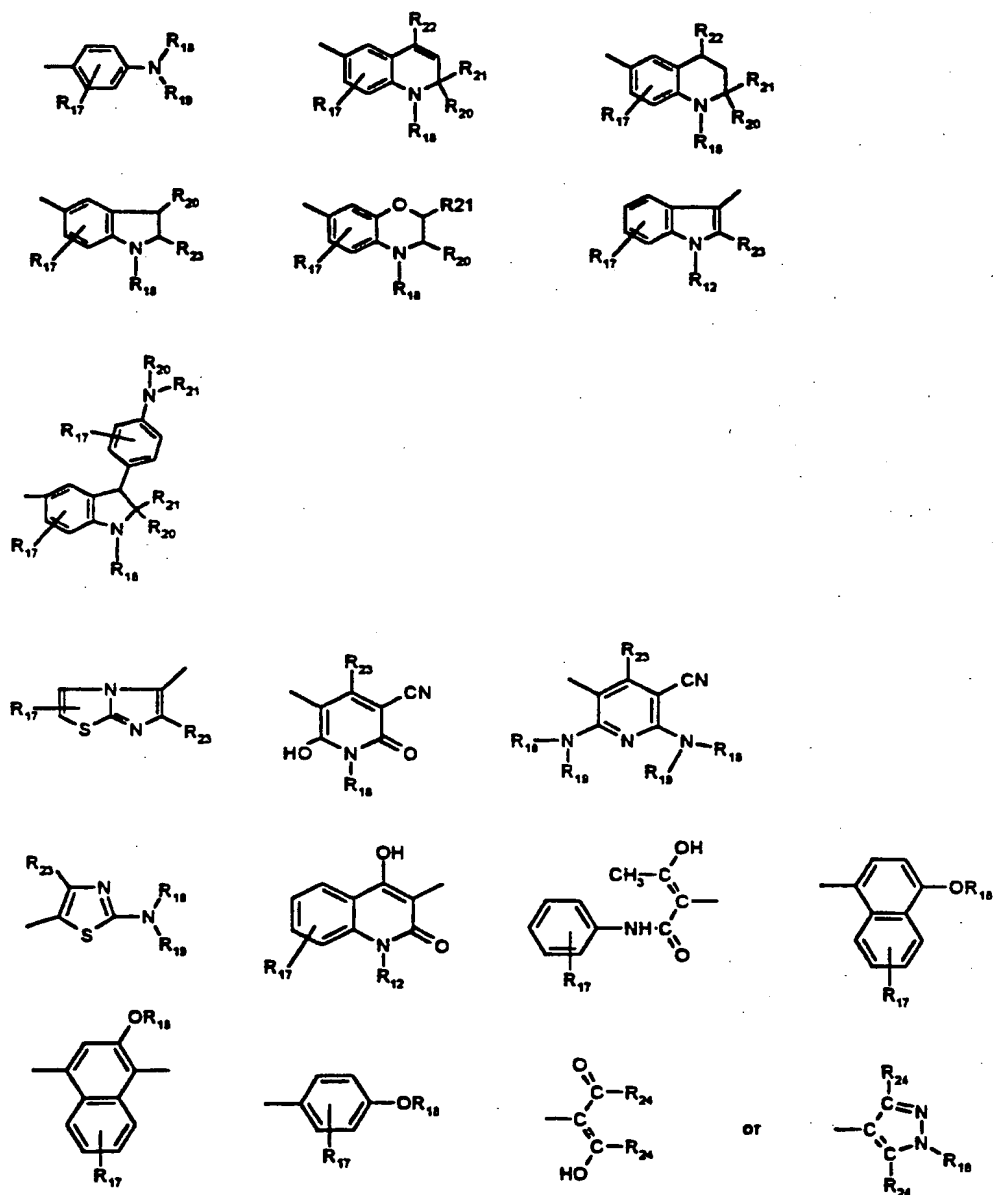
tetrahydrofurfurylamino, 4-(hydroxymethyl)
cyclohexanemethylamino,



- 5 or hydroxy; Q and Q' are independently selected from-O-,
-N(COR₁₀)-, -N(SO₂R₁₀)-, -N(R₁₀)-, -S-, -SO₂-, -CO₂-,
-CON(R₁₀)-, SO₂N (R₁₀)-, wherein R₁₀ is selected from
hydrogen, aryl, C₃-C₈ cycloalkyl, or C₁-C₁₀ alkyl; R₁₅ is
10 selected from hydrogen, cyano, C₁-C₆ alkylamino, C₁-C₆
alkoxy, halogen, arylthio, aryl, heteroaryl,
heteroarylthio, C₁-C₆ alkoxy carbonyl, aroyl or
arylsulfonyl; R₁₆ is selected from hydrogen, C₁-C₁₀ alkyl,
C₃-C₈ cycloalkyl and aryl; R₁₆' is selected from the group
15 consisting of hydrogen, one or two groups selected from
C₁-C₆ alkyl, halogen and C₁-C₆ alkoxy; wherein each C₁-C₆
alkyl group and C₁-C₆ alkyl group which is a portion of
another group may contain at least one substituent
selected from hydroxy, cyano, chlorine, fluorine, C₁-C₆
20 alkoxy, C₃-C₈ cycloalkoxy, C₁-C₆ alkylcyclohexyl,
hydroxymethyl cyclohexyl, aryl and heteroaryl; with the
provision that two acidic groups containing one acidic
proton each or one acidic group containing two acidic
hydrogens be present in the compounds of Formula XIV-
25 XIXf.

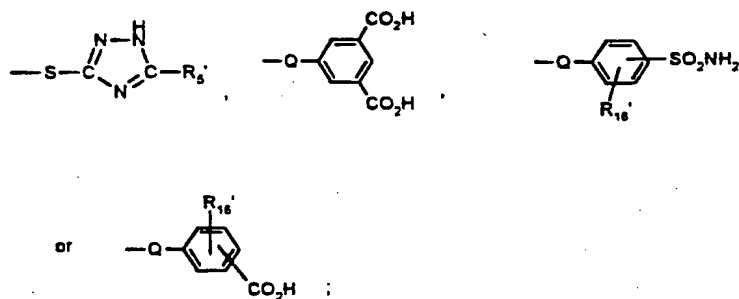
Typical coupler residues which are represented by Z
above in Formulae VI, VII, XIII for the classes of azo,
disazo and azo-methine compounds, respectively include:

- 22 -

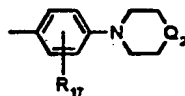


- 23 -

- alkoxy, C₁-C₆ alkylthio, -O-C₂-C₆ alkylene-OH, O-C₂-C₆ alkylene-C₁-C₆ alkanoyloxy, C₁-C₆ alkylene-OH, C₁-C₆ alkylene-C₁-C₆ alkanoyloxy, halogen, carboxy, C₁-C₆ alkoxycarbonyl, trifluoromethyl, NHCOR₂₄, NHCO₂R₂₄, NHCON(R₂₄)R₂₅, and NHSO₂R₂₅, wherein R₂₄ is selected from hydrogen, C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl, R₂₅ is selected from C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl wherein each C₁-C₁₀ alkyl group in R₂₄ and R₂₅ may be further substituted with one or more groups selected from C₃-C₈ cycloalkyl, aryl, aryloxy, arylthio, CO₂H, CO₂ C₁-C₆ alkyl, cyano, hydroxy, succinimido, C₁-C₆ alkoxy,



- wherein R₅', R₁₆' and Q are as defined above; R₁₈ and R₁₉ are independently selected from hydrogen, unsubstituted C₁-C₁₀ alkyl, substituted C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl, C₃-C₈ alkenyl, C₃-C₈ alkynyl and aryl or R₁₈ and R₁₉ may be combined with another element to which they are attached to form a radical Z having the formula

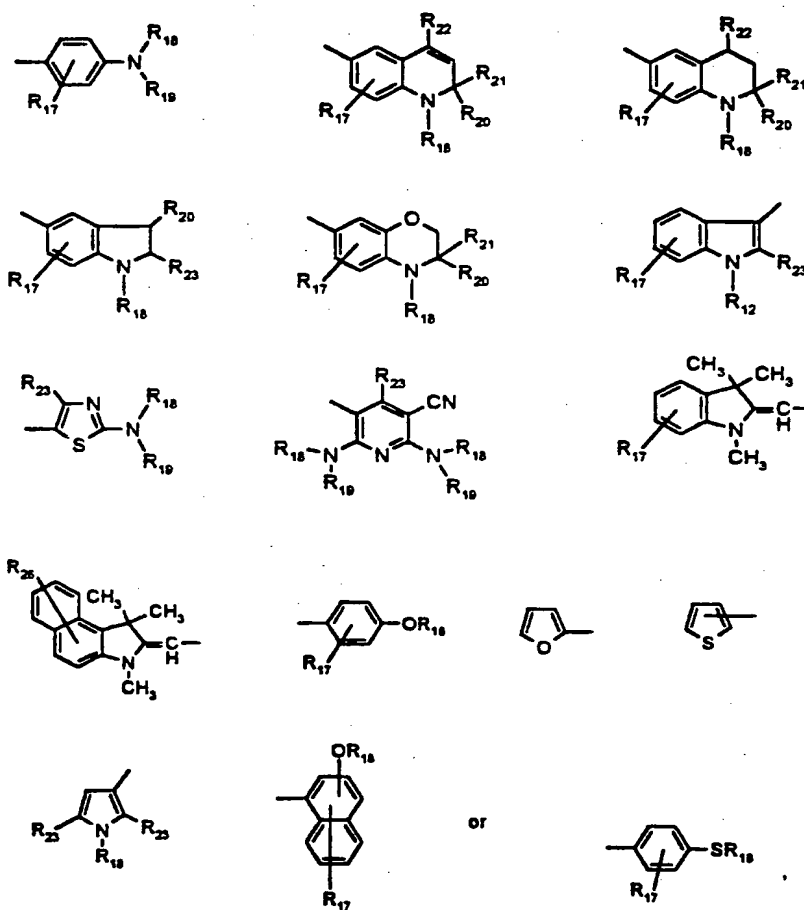


- wherein Q₂ is selected from a covalent bond, -O-, -S-, -SO₂-, -CO-, -CO₂-, -N-(C₁-C₆ alkyl)-, -N(CO C₁-C₆ alkyl)-, -N(SO₂ C₁-C₆ alkyl)-, -N(CO aryl)-, or -N(SO₂ aryl); R₂₀, R₂₁

- 24 -

and R_{22} are independently selected from the group consisting of or C_1 - C_6 alkyl; R_{23} is selected from hydrogen, C_1 - C_6 alkyl, C_3 - C_8 cycloalkyl, heteroaryl or aryl.

- 5 Typical electron, rich aromatic residues which are represented by R_{11} in Formulae VIII- XII include:



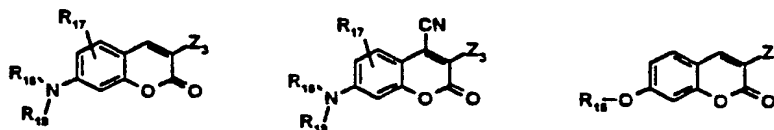
wherein R_{26} is selected from the group consisting of hydrogen, a group selected from C_1 - C_6 alkoxy, CO_2H ,

- 25 -

C₁-C₆ alkyl or C₁-C₆ alkoxy; wherein R₁₇-R₂₃ are as defined previously.

Preferred coumarin compounds useful in the practice of the invention correspond to the following formulae:

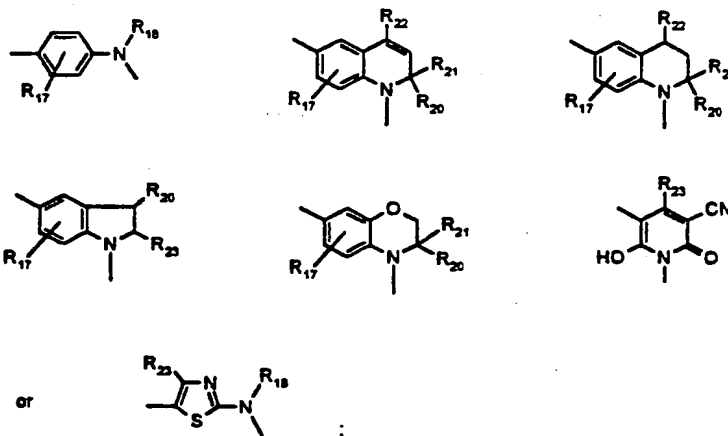
5



wherein Z₃ is selected from cyano, C₁-C₆ alkoxy, carbonyl, C₁-C₆ alkylsulfonyl, arylsulfonyl, aryl, heteroaryl, formyl, aroyl, C₁-C₆ alkanoyl or -CH=D, wherein D, R₁₇, R₁₈ and R₁₉ are as defined previously with the provision that the coumarin compounds contain two acidic functional groups containing one acidic hydrogen each or contain one sulfamoyl (-SO₂NH₂) group which contains two acidic hydrogens.

15

Typical coupler residues which are represented by Y₁ in Formula VIIa above include those of the formula (Z₁-L₁-Z₂) wherein Z₁ and Z₂ are independently selected from



or

20

- 26 -

- wherein L_1 is bonded to the nitrogen atom of Z_1 and Z_2 ;
 wherein L_1 is selected from C_2 - C_{12} alkylene, C_3 - C_8
 cycloalkylene, arylene, C_1 - C_4 alkylene- C_3 - C_8 cycloalkylene-
 C_1 - C_4 alkylene, C_1 - C_4 alkylene-arylene- C_1 - C_4 alkylene, C_2 - C_4
 5 alkylene-O-arylene-O- C_2 - C_4 alkylene, - C_2 - C_4 alkylene O_{1-3} -
 C_2 - C_4 alkylene, C_2 - C_4 alkylene-S- C_2 - C_4 alkylene, C_2 - C_4
 alkylene-SO₂- C_2 - C_4 alkylene, C_2 - C_4 alkylene-N(SO₂ C_1 - C_6
 alkyl)- C_2 - C_4 alkylene, C_2 - C_4 alkylene-N(SO₂ aryl)- C_2 - C_4
 alkylene, C_2 - C_4 alkylene-OCO₂- C_2 - C_4 alkylene, C_2 - C_4
 10 alkylene-O₂C-arylene-CO₂- C_2 - C_4 alkylene, C_2 - C_4 alkylene-O₂C-
 C_1 - C_{12} alkylene-CO₂- C_2 - C_4 alkylene, C_2 - C_4 alkylene-O₂C- C_3 - C_8
 cycloalkylene-CO₂- C_2 - C_4 alkylene, C_2 - C_4 alkylene-NHCO- C_2 - C_4
 alkylene and C_2 - C_4 alkylene-NHSO₂- C_2 - C_4 alkylene; wherein
 R_{17} , R_{18} , R_{20} , R_{21} , R_{22} , and R_{23} are as defined previously.
- 15 In the above definitions it is intended that in the
 terms C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_1 - C_6 alkoxycarbonyl, C_1 - C_6
 alkylthio, C_1 - C_6 alkylsulfonyl, C_1 - C_6 alkanoyl, -CONH C_1 - C_6
 alkyl, -SO₂NH C_1 - C_6 alkyl, -CON(C_1 - C_6 alkyl)₂, -SO₂N(C_1 - C_6
 alkyl)₂, -NHSO₂ C_1 - C_6 alkyl, -N(C_1 - C_6 alkyl) SO₂ C_1 - C_6 alkyl,
 20 etc. unless otherwise stated that the C_1 - C_6 alkyl portion
 of the group refers to a straight or branched chain alkyl
 group containing one to six carbon atoms and these
 substituted with one or more groups selected from carboxy,
 cyano, -SO₂NH₂, SO₂NH C_1 - C_6 alkyl, cyano, fluorine,
 25 chlorine, C_1 - C_6 alkoxy, aryloxy, aryl, heteroaryl,
 arylthio, heteroarylthio, C_3 - C_8 -cycloalkyl, -O₂C C_1 - C_6
 alkyl or -CO₂ C_1 - C_6 alkyl.
- The terms C_1 - C_4 alkylene, C_2 - C_4 alkylene, C_1 - C_6
 alkylene, C_2 - C_6 alkylene, and C_2 - C_{12} alkylene are used to
 30 refer to divalent aliphatic hydrocarbon radicals
 containing one to four carbon atoms, two to four carbon
 atoms one to six carbon atoms, two to six carbon atoms, or
 two to twelve carbon atoms, respectively, and these
 optionally substituted with one or more groups selected
 35 from C_1 - C_6 alkoxy, hydroxy, -O₂C C_1 - C_6 alkyl, carboxy, CO₂
 C_1 - C_6 alkyl, chlorine, fluorine, aryl or aryloxy.

- 27 -

The terms C₃-C₈ cycloalkyl and C₃-C₈ cycloalkylene are used to refer to fully saturated monovalent and divalent cycloaliphatic radicals, respectively, and these substituted by one or more C₁-C₆ alkyl groups.

- 5 The terms C₃-C₈ alkenyl and C₃-C₈ alkynyl are used to refer to straight or branched hydrocarbon radicals containing at least one double bond or at least one triple bond, respectively.

- 10 In the terms aryl, NH aryl, aryloxy, aroyl, arylthio, arylsulfonyl, aryloxysulfonyl, -N(SO₂ aryl)-, -N(CO aryl)-, NHCO aryl, -NH CONH aryl, NHSO₂, aryl, etc., the aryl portion of the group represents phenyl and naphthyl and these substituted with one or more groups selected from -CO₂H, C₁-C₆ alkyl, CO₂ C₁-C₆ alkyl, SO₂NH₂,
15 SO₂NH C₁-C₆ alkyl, hydroxy, O C₁-C₆ alkyl, S C₁-C₆ alkyl, phenyl, O-arylene-CO₂H, -S-arylene-CO₂H, SO₂ arylene-CO₂H, halogen, NHSO₂ C₁-C₆ alkyl, trifluoromethyl, NH CO C₁-C₆ alkyl, cyano, or 1(H)-1,2,4-triazol-3-ylthio.

- 20 The term arylene is used to represent 1,2-, 1,3-, and 1,4- phenylene and these optionally substituted with one or more groups mentioned above as possible substituents on the aryl radical.

- 25 The term "heteroaryl" is used to describe a 5 or 6 membered heterocyclic aromatic ring containing one oxygen atom, and/or one sulfur atom, and/or up to three nitrogen atoms, said heterocyclic aryl ring optionally fused to one or two phenyl rings or another 5 or 6-membered heteroaryl ring. Examples of such ring systems include thienyl, furyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl,
30 isothiazolyl, oxazolyl, isoxazolyl, triazolyl, thiadiazolyl, oxadiazolyl, tetrazolyl, thiatriazolyl, oxatriazolyl, pyridyl, pyrimidyl, pyrazinyl, pyridazinyl, thiazinyl, oxazinyl, triazinyl, thiadiazinyl, oxadiazinyl, dithiazinyl, dioxazinyl, oxathiazinyl, tetrazynyl,
35 thiatriazinyl, oxatriazinyl, dithiadiazinyl, imidazolinyl, dihydropyrimidyl, tetrahydropyrimidyl, tetrazolo [1,5-b]-

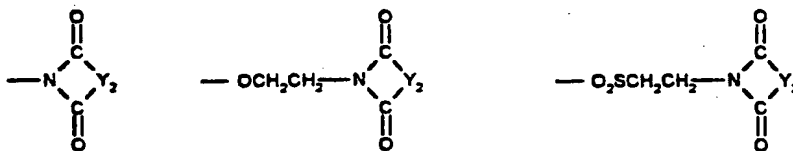
- 28 -

pyridazinyl and purinyl, benzoxazolyl, benzothiazolyl, benzimidazolyl, indolyl, and the like and those rings substituted with one or more substituents listed above in the definition of the term "aryl".

5 The term halogen is used to refer to fluorine, chlorine, bromine and iodine.

In the above definitions the unsubstituted and substituted C₁-C₁₀ alkyl groups or portion of groups mentioned refer to fully saturated hydrocarbon radicals containing one to ten carbon atoms, either straight or
10 branched chain, and such alkyl radicals substituted with one or more of the following: C₃-C₈ cycloalkyl, aryl, hydroxy, cyano, -O-C₂-C₄ alkylene OH, -O-C₂-C₄ alkylene O₂ C-C₁-C₆ alkyl, -S-C₂-C₄ alkylene-OH, chlorine, fluorine,
15 -O-C₁-C₆ alkyl, -O-aryl, -SO₂ aryl, -SO₂-C₁-C₆ alkyl, 2-pyrrolidino, phthalimidino, phthalimido, succinimido, glutarimido, o-benzoic sulfimide, vinyl sulfonyl, -NHCO C₁-C₆ alkyl, NHCOH, -NHSO₂-C₁-C₆ alkyl, NHSO₂ aryl, -NHCO aryl, -NH-CO₂-C₁-C₆ alkyl, -SO₂NH₂, -SO₂-NH-C₁-C₆ alkyl,
20 -SO₂N-(C₁-C₆ alkyl)₂, -CO₂-C₁-C₆ alkyl, CONH₂, -CONH-C₁-C₆ alkyl, -CO₂-aryl, -CON(C₁-C₆ alkyl)₂, -CONH aryl, -CONH(C₁-C₆ alkyl) aryl, -SO₂N(C₁-C₆ alkyl) aryl, -SO₂-NH-C₃-C₈ cycloalkyl, -CONH-C₃-C₈ cycloalkyl, -OCO₂-C₁-C₆ alkyl, -O C₂-C₄ alkylene CN; groups of the formulae:

25

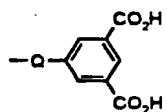
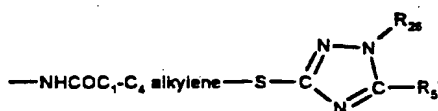
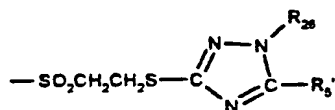
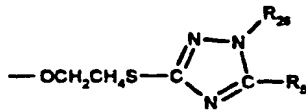
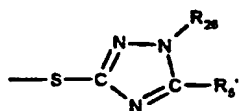


wherein Y₂ is selected from 1,2-phenylene; 1,2 pheylene substituted with C₁-C₆ alkyl, C₁-C₆ alkoxy, halogen, -CO₂H,
30 -CO₂ C₁-C₃ alkyl or nitro; C₂-C₄ alkylene, vinylene, -O CH₂- , -SCH₂-, -CH₂OCH₂-, -OCH₂CH₂-, -CH₂SCH₂-, -NHCH₂-,

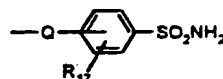
- 29 -

-NHCH₂CH₂-, -N(C₁-C₆ alkyl)CH₂-, NHC(C₁-C₆ alkyl)₂-, -N(C₁-C₆ alkyl)CH₂CH₂ or -NHC(aryl)₂-; groups of the formulae:

-SR₂₅-, -SO₂CH₂CH₂SR₂₅-, -OCH₂CH₂SR₂₅-,



or



5

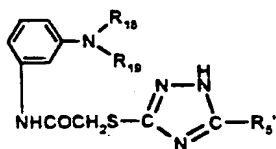
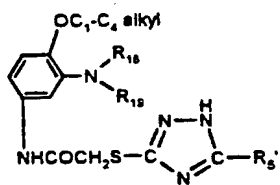
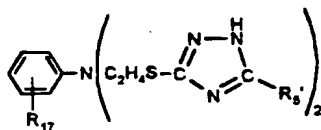
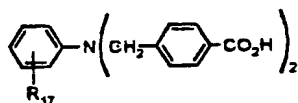
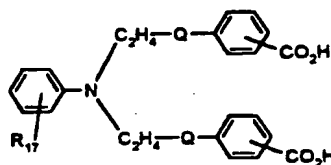
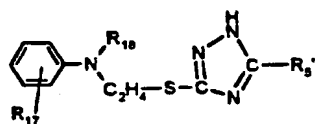
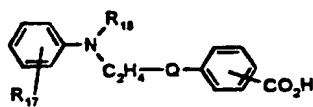
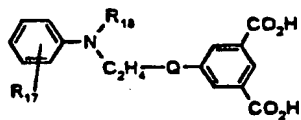
wherein R₂₆ is selected from hydrogen, C₁-C₁₀ alkyl, C₂-C₄ alkylene-OH, C₂-C₄ alkylene-CO₂H, C₂-C₄ alkylene-CO₂ C₁-C₆ alkyl, chloro, C₁-C₆ alkoxy, C₁-C₄ alkylene-arylene-CO₂H, C₂-C₄ alkylene-O-arylene-CO₂H or C₂-C₄ alkylene-S-arylene-CO₂H and R₅' R₁₇, R₂₅ and Q are as defined previously:

The term "light absorbing" is used to indicate the property of absorbing near ultra violet, visible or near infrared light, more particularly absorbing light between the wavelengths of 300-1200 nm, preferably between about 325 nm and 1100 nm, and most preferably between about 325 nm and 1000 nm.

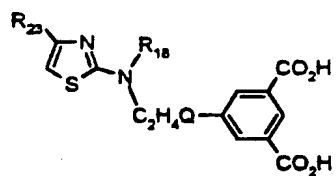
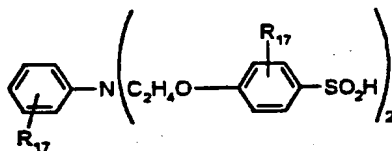
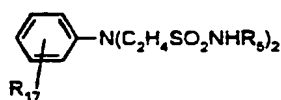
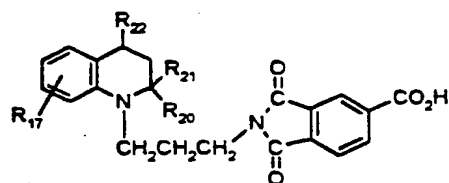
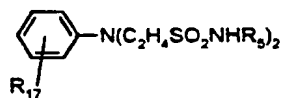
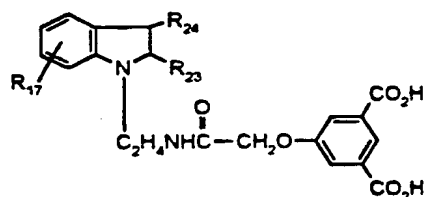
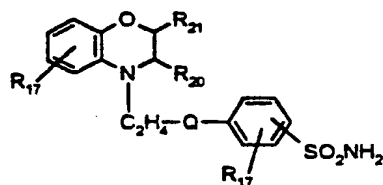
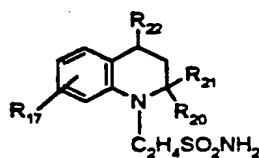
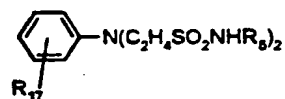
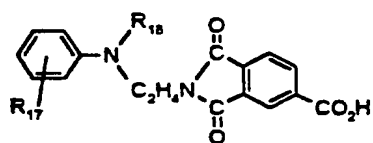
Typical aromatic amines which are useful as the coupling components to prepare compounds of Formulae VI, VII and VIII and as intermediates for preparing the compounds of Formula VIII, VIIIa, IX, X, XI and XII are as follows:

20

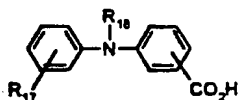
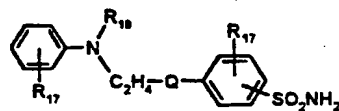
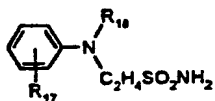
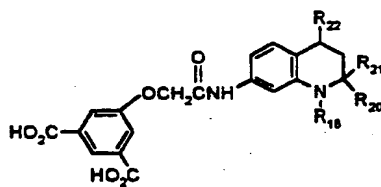
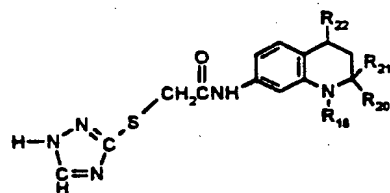
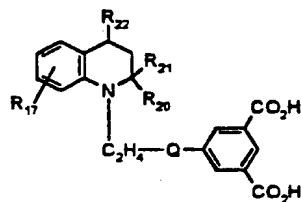
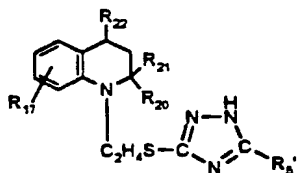
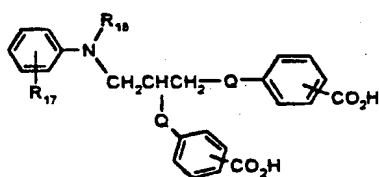
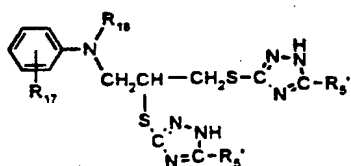
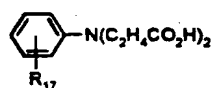
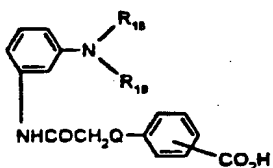
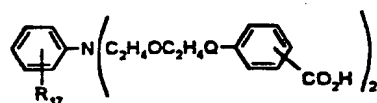
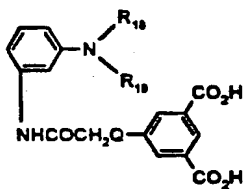
- 30 -



- 31 -



- 32 -



- 33 -

wherein Q, R₅', R₁₇, R₁₈, R₁₉, R₂₀, R₂₁, R₂₂ and R₂₃ are as defined previously.

5 Typical diazotizable amines (R₆ NH₂) useful in the preparation of azo, disazo and bis-azo compounds of Formulae VI, VII, and VIIa, respectively, are adequately disclosed in the literature, e.g.:

M. Weaver and L. Shuttleworth, Dyes and Pigments, 3 (1982) 81-121;

10 L. Shuttleworth and M. Weaver, Chem. Appl. Dyes, 1990, 107-63, edited by D. Waring and G. Hallas, Plenum, New York, N.Y.;

U.S. Pat. Nos. 3,438,961; 3,573,273; 3,639,384;
3,707,532; 3,790,557; 3,816,388; 3,816,392; 3,878,189;
15 3,980,634; 4,012,372; 4,039,522; 4,049,643; 4,083,684;
4,083,844; 4,097,475; 4,105,655; 4,119,621; 4,140,683;
4,180,503; 4,189,428; 4,207,233; 4,211,696; 4,264,495;
4,283,332; 4,400,318; 4,431,585; 4,456,551; 4,487,719;
4,542,207; 4,564,673; 4,619,991; 4,621,136; 4,650,861;
20 4,668,775; 4,734,490; 4,751,288; 4,760,133; 4,764,600;
4,837,269; 4,841,036; 4,843,153; 4,888,432; 4,960,874;
5,037,966; 5,132,411; 5,144,015; 5,283,326; 5,296,325;
5,352,774.

Typical coupling components H-Z useful in preparing
25 azo compounds, disazo and azo-methine compounds of Formula VI, VII and XIII, respectively, are disclosed in the literature, e.g: H. R. Schwander, Dyes and Pigments, 3(1982) 133-160; L. Shuttleworth and M. Weaver, Chem. Appl. Dyes, 1990, 107-63, edited by D. Waring and G.
30 Hallas, Plenum, New York, NY; U.S. Patent No. 3,639,384;
3,639,385; 3,657,215; 3,673,169; 3,816,388; 3,829,410;
3,919,188; 3,950,130; 3,980,634; 4,041,025; 4,097,475;
4,119,621; 4,179,435; 4,234,482; 4,283,332; 4,341,700;
4,400,318; 4,431,585; 4,396,547; 4,619,992; 4,642,339;
35 4,650,861; 4,668,775; 4,764,600; 4,837,269; 4,843,153;
5,235,047; 5,283,326; 5,352,774.

- 34 -

Typical active methylene compounds useful in the preparation of methine, arylidene, polymethine, azamethine and azo-methine compounds corresponding to Formulae VIII, VIIIA, VIIIB, IX and XIII, respectively, are disclosed in the literature, e.g. U.S. Pat. Nos. 4,338,247; 4,617,373; 4,617,374; 4,707,537; 4,749,774; 4,826,903; 4,845,187; 4,950,732; 4,981,516 and 5,283,326.

According to the present invention the light-absorbing polymeric compositions are incorporated into a wide variety of thermoplastic polymers using conventional techniques, e.g. solution or melt blending, such as those employed to incorporate other additives in such polymers (see R. Gächter and H. Müller, Editors: *Plastics Additives Handbook*, Hansu Publishers, New York, 1985, pp. 507-533; 729-741). For example, the light absorbing polymeric compositions may be dry blended in the form of pellets or powders with or without adhesion promoters or dispersing agents. This premix can be subsequently processed on extruders or injection molding machines. Other conventional additives such as plasticizers, nucleating agents, flame retardants, lubricants, etc. may also be present in the final thermoplastic composition.

A wide range of thermoplastic polymers useful for blending with the light absorbing polymeric compositions are known in the art and includes the homopolymers, copolymers and blends of polyesters, e.g., poly(ethylene terephthalate); polyolefins, e.g., polypropylene, polyethylene, linear low density polyethylene, polybutylene, and copolymers made from ethylene, propylene and/or butylene; copolymers from acrylonitrile, butadiene, and styrene; copolymers from styrene and acrylonitrile; polyamides, e.g., Nylon 6 and Nylon 66; polyvinyl chloride; polyurethanes; polyvinylidene chloride; polycarbonates; cellulose esters, e.g., cellulose acetate, propionate, butyrate, or mixed esters; polyacrylates,

- 35 -

e.g., poly(methyl methacrylate); polyimides; polyester-amides; polystyrene; and mixtures or blends thereof etc.

It should also be appreciated that a multiplicity of colors may be obtained by combining individual colors,

- 5 e.g., subtractive colors such as yellow, magenta and cyan according to known color technology (see N. Ohta, *Photographic Science and Engineering*. Volume 15, No. 5, Sept.- Oct. 1971, pp. 395-415).

- 10 The particular chromophore groups present will, of course, determine the color (hue + value + chroma) of the colored polymer composition and finally the color (hue + value + chroma) of the thermoplastic polymer blends of the present invention. A large gamut of colors may be obtained, as noted above.

- 15 The actual amount of the light absorbing polymers used in combination with thermoplastic polymer will depend upon the inherent tinctorial strength of the chromophore used to prepare the light absorbing polymer, the mole % of the light absorbing monomer used to prepare the light
20 absorbing polymer and the required level of light absorption necessary to achieve a certain property. Typically, the amount of light-absorbing polymer added to the thermoplastic polymer is such that the total amount of light-absorbing polymer in the final thermoplastic blend
25 is from about .001% by weight to about 20% by weight, preferably from about 0.01% by weight to about 10% by weight. The final thermoplastic polymer blends thus provided are useful as a variety of molded and extruded articles, including thick and thin plastic films, plastic
30 sheeting, molded plastic articles, containers and fibers, and the like.

- When the light-absorbing polymeric compositions absorb visible light they may be used to impart light or heavy shades of a variety of colors to thermoplastics.
35 Certain compounds which possess unique visible light-absorbing properties are useful also as toners in

- 36 -

imparting a desirable neutral to slightly blue hue to polyesters having a yellow appearance as described in U.S. Patent 5,384,377, which discloses the copolymerization of certain thermally stable colorants for this purpose during polyester manufacture. Some of the infra-red absorbing polymeric compositions are useful in imparting invisible markings to thermoplastics as described in U.S. Pat. No. 5,461,136, wherein the infrared absorbing compounds are fluorescent in the near infrared and are copolymerized into the thermoplastic condensation polymer during manufacture. The ultra violet absorbing polymeric compositions may be used to impart ultra violet (UV) light screening properties to the thermoplastics; to serve as optical brighteners for the thermoplastics or to serve as UV stabilizers for the polymers themselves or for other light absorbers such as colorants.

The weight average molecular weights (Mw) and the number average molecular weights (Mn) of the polymeric compositions were determined using gel permeation chromatography (GPC) analysis.

The following examples illustrate further the practice of the invention.

Example 1

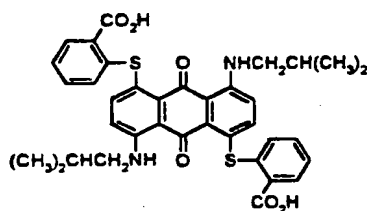
A mixture of 1,5-bis(2-carboxyphenylthio) anthraquinone (25.60 g, 0.05 mole), 1,2-ethanediol, dimethanesulfonate (10.90 g, 0.05 mole), potassium carbonate (13.82 g, 0.10 mole) and N-methyl-2-pyrrolidinone (NMP) (400 mL) was heated with stirring at 125°C for 1.0 hr. The reaction mixture was poured into methanol (600 mL) with stirring. The yellow polymeric product was collected by filtration and washed with methanol until filtrate was essentially clear. The methanol- wet filter cake was slurried in 1.0 L of water, the mixture acidified by the addition of acetic acid and

- 37 -

the yellow product was collected by filtration, washed with hot water and dried in air (yield- 21.16 g). By gel permeation chromatography (GPC) the polymeric product has a weight average molecular weight of 6,083, and number average molecular weight of 3,000 and a polydispersity value of 2.03.

Example 2

A mixture of a blue anthraquinone compound (19.65 g 0.03 mole) containing two carboxy groups and having the following structure:



1,2-ethanediol, dimethanesulfonate (6.54g, 0.03m), potassium carbonate (8.28 g, 0.06 mole) and N,N-dimethylformamide (DMF) (100 mL) was heated with stirring at about 95°C for 1.5 hr. The reaction mixture became too thick to stir effectively and additional DMF (50 mL) was added to facilitate stirring. Stirred about 15 min. longer at about 95°C, and then added methanol (100 mL) with good stirring to the slightly cooled reaction mixture. The blue polymeric product was collected by filtration and washed with methanol. The methanol-wet filter cake was added to water (600 mL) and the mixture was acidified with acetic acid, and then the polymeric product was collected by filtration, washed with water and dried in air (yield 18.18 g). By GPC analysis the blue polymer had a molecular weight average of 3,038, a number average molecular weight of 1,814 and a polydispersity of 1.67.

- 38 -

Example 2a

A mixture of 1,5-bis (isobutylamino)-4,8-dibromoanthraquinone (25.3 g, 0.05 mole), thiosalicylic acid (23.1 g, 0.15 mole), anhydrous K₂CO₃ (20.7 g, 0.15 mole), cupric chloride dihydrate (1.2 g) and DMF (250 mL) was heated at 90-95°C with stirring for 2.0 hours. Thin layer chromatography (TLC) using 1:1 tetrahydrofuran (THF): cyclohexane showed complete conversion of the red starting material to the desired blue polar product. The reaction mixture was allowed to cool and then was drowned into water (800 mL). The blue solid was precipitated by acidification with acetic acid with stirring. The mixture was heated to about 60°C with occasional stirring and the solid was collected by filtration, washed with hot water and dried in air. Further purification was accomplished by reslurrying the product in hot methanol (300 mL), allowing to cool to room temperature, collecting by filtration, washing with methanol and air drying to yield the starting material (31.5 g) for Example 2.

Example 2b

1,5-Bis(isobutylamino)anthraquinone (28.0 g, 0.08 mole) was added to DMF (300 mL) and the mixture stirred at room temperature. A solution of 1,3-dibromo-5,5-dimethylhydantoin (23.0 g, 0.08 m) dissolved in DMF (75.0 mL) was added dropwise to the reaction mixture while warming to about 50°C. After complete addition of the brominating agent, the reaction mixture was heated at 50-60°C for 1.5 hours, allowed to cool and then drowned by gradual addition to water (500 mL) with stirring. The red product was collected by filtration, washed with water and dried in air. The yield of product was 39.6 g and field desorption mass spectrum analysis (FDMS) showed the product to be 1,5-bis(isobutylamino)-4,8-

- 39 -

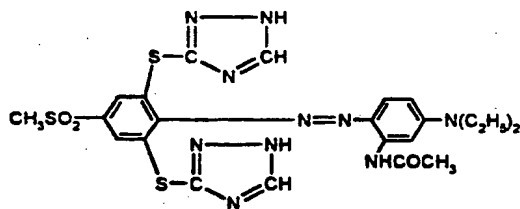
dibromoanthraquinone used as the intermediate in Example 2a.

Example 2c

- 5 A mixture of 1,5-dichloroanthraquinone (69.5 g, 0.25 mole), isobutylamine (100 g, 1.4 mole) and 2-ethoxyethanol (400 mL) was heated at reflux for 36.0 hours and allowed to cool. Methanol (400 mL) was added to make the mixture containing the crystallized product more stirrable. The
- 10 dark red product was collected by filtration, washed with methanol, reslurried in hot methanol and allowed to cool, collected by filtration, washed with methanol and dried in air (yield - 67.7 g). FDMS showed the product to be the 1,5-bis(isobutylamino)anthraquinone in high purity which
- 15 was used as the starting material for Example 2b.

Example 3

- A mixture of an azo compound (2.93 g, 0.005 m) containing two 1(H)-1,2,4-triazol-3-thio groups and having
- 20 the following structure:



- 1,2-ethanediol, dimethanesulfonate (1.08 g, 0.005 mole),
- 25 potassium carbonate (1.50 g) and DMF (25.0 mL) was heated at about 95°C with stirring for 2.5 hrs. The reaction mixture was drowned into methanol (150 mL) and the red polymeric product was collected by filtration, washed with water containing a little acetic acid and then washed with
- 30 hot water and dried in air (yield- 2.35 g). The polymer by GPC analysis had a weight average molecular weight of

- 40 -

5,396, a number average molecular weight of 3,044 and a polydispersity value of 1.77.

Example 4

5 Eastar® PETG copolyester 6763, a poly(ethylene-1,4-cyclohexanedimethylene) terephthalate, (Eastman Chemical Co.) (400 g. of previously dried pellets) was dry blended with the yellow anthraquinone polymeric composition (0.12 g) of Example 1. The blend was extruded with a C. W. 10 Brabender $\frac{3}{4}$ in. extruder, equipped with a mixing screw, at 250°C into a water bath and the extrudate pelletized.

The pellets were redried at 70°C for about 17 hrs. at a pressure of about 1-5 torr. A portion of the dried pellets (1.40g) was pressed into a 18-20 mil film at 250°C 15 using a 2-inch diameter circular mold in a Pasadena Hydraulic, Inc. press using 12,000 pounds ram force (4 inch ram). A transparent yellow film was produced with excellent color development, which contained about 300 ppm by weight of the yellow polymeric composition.

20

Example 5

Example 4 was repeated using 0.12 g of the blue anthraquinone polymeric composition of Example 2 to give a bright blue transparent copolyester film with good color 25 development.

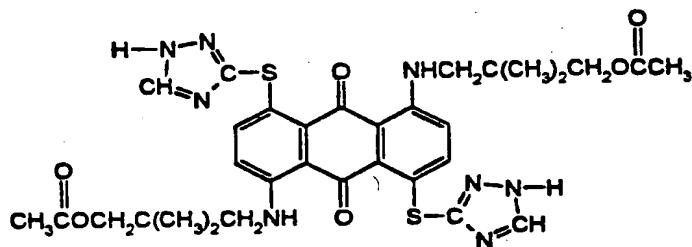
Example 6

Example 4 was repeated using 0.12 g of the red azo polymeric composition of Example 3 to produce a bright red 30 transparent film having good color development.

Example 7

A mixture of a blue anthraquinone compound (3.46 g, 0.005 35 mole) containing two acidic 1(H)-1,2,4-triazol-3-ylthio groups and having the following structure

- 41 -



1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole) DMF (30 mL) and potassium carbonate (1.5 g) was heated
 5 with stirring at about 95°C for 2.0 hours and then drowned into methanol (100 mL). The blue polydye was collected by filtration and washed with methanol. The methanol-wet cake was reslurried in water (400 mL) and the stirred mixture was acidified by addition of acetic acid and
 10 heated to about 60°C. The final polymeric product was collected by filtration, washed with water and dried in air (yield - 1.5 g). Absorption maxima were observed at 594, 636 nm in a solution of DMF in the visible light absorption spectrum. By GPC, the polydye has a weight
 15 average molecular weight (Mw) of 3,769, a number average molecular weight (Mn) of 2,119 and a polydispersity of 1.78.

Example 7a

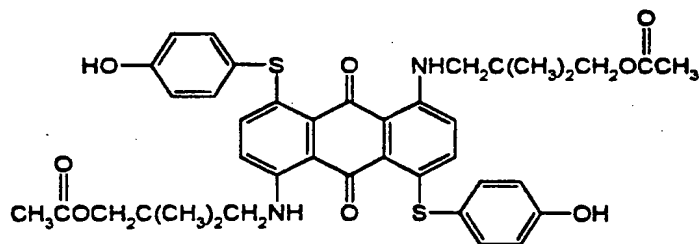
20 A mixture of 1,5-bis[(3-acetoxy-2,2-dimethylpropyl)amino-4,8-dibromoanthraquinone (6.50 g, 0.01 mole) (product of Example 2 - Invention Report Docket No. 70524), 3-mercapto-1(H)-1,2,4-triazole (3.03 g, 0.03 mole),
 25 potassium carbonate (4.15 g, 0.03 mole), cupric chloride dihydrate (0.65 g) and DMF (100 mL) was heated 14 hours at about 100- 105°C. The reaction mixture was drowned into a mixture of water (400 mL) and 10% aqueous solution of hydrochloric acid (200 mL). The blue product was

collected by filtration, washed with hot water and dried in air (yield - 6.58 g). FDMS supported the desired structure of the starting anthraquinone compound for Example 7.

5

Example 8

A mixture of blue anthraquinone compound (2.48 g, 0.0033
10 mole) having the following structure



1,2-ethanedithiol, dimethanesulfonate (0.73 g, 0.0033 mole), potassium carbonate (0.5 g) and DMF (30.0 mL) was heated at about 95°C for 3.0 hours. The reaction mixture was drowned into methanol (150 mL) with stirring and the blue polydye product was collected by filtration and washed with methanol. The methanol-wet cake was reslurried in water (200 mL) and the mixture acidified with acetic acid. Collecting the blue solid by filtration, washing with hot water and air drying gave 1.21 g of polydye product, which has absorption maxima at 606,652 nm in DMF in the visible absorption spectrum, a weight average molecular weight of 4,453, a number average molecular weight of 2,721 and a polydispersity of 1.6.

Example 8a

- 43 -

A mixture of 1,5-bis[(3-acetoxy-2,2-dimethylpropyl)amino]-4,8-dibromoanthraquinone (19.56 g, 0.03 mole), p-hydroxybenzenethiol (17.64 g, 0.14 mole), potassium carbonate (19.32 g, 0.14 mole), cupric chloride dihydrate (1.0 g) and DMF (150 mL) was heated and stirred at 90-95°C for 7.0 hours and then at 120°C for about 2.0 additional hours. TLC (50:50 THF: cyclohexane) showed mostly the desired blue product, but still a small amount of violet half-reacted product was present. The reaction mixture was drowned into methanol (500 mL) and the mixture allowed to cool. After crystallization, the blue solid was collected by filtration, washed with methanol, washed with hot water and then dried in air (yield - 17.6 g). FDMS supported the desired structure of the starting anthraquinone compound for Example 8. In the visible light absorption spectrum in DMF, a maximum absorbance (λ_{max}) was observed at 652 nm (extinction coefficient ϵ of 24,638).

20

Example 9

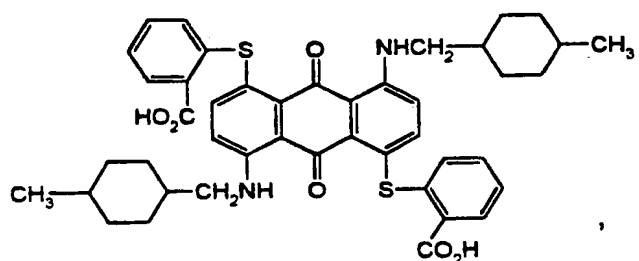
A mixture of 1,4-bis-(2,6-dimethyl-4-hydroxyanilino)anthraquinone (4.78 g, 0.01 mole) (Synthesis Example 1 of U. S. Patent 3,918,976), 1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole), potassium carbonate (3.0 g) and DMF (60 mL) was heated at 90-95°C with stirring for 4.0 hours. After drowning the reaction mixture into methanol (300 mL), the product was collected by filtration and washed with methanol until filtrate was essentially colorless. The methanol-wet cake was reslurried in 100 mL water and acidified by adding acetic acid with stirring. After heating to about 50°C, the product was collected by filtration, washed with hot water and dried in air (yield - 1.2 g). By GPC, the blue polydye had a weight average molecular weight (M_w) of

35

2,764, a number average molecular weight (M_n) of 1,607 and a polydispersity of 1.72. In DMF, the visible light absorption maxima were at 586, 630 nm.

5 Example 10

A mixture of an anthraquinone diacidic compound (1.52 g, .002 mole) having the following structure



10

1,2-ethanediol, dimethanesulfonate (0.44 g, 0.002 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at about 95°C with occasional stirring for 20 hours. The reaction mixture was downed into methanol (50 mL) and the product was collected by filtration, washed with methanol, water plus acetic acid, hot water and then dried in air (yield - 1.05 g). The blue polydye had a weight average molecular weight (Mw) of 3,586, a number average molecular weight (Mn) of 1,867 and a polydispersity value of 1.92. In the visible light absorption spectrum, maxima of absorbance occurred at wavelengths of 605 and 647 nm in DMF.

25 Example 10a

- 45 -

A mixture of 1,5-bis-(4-methylcyclohexanemethylamino)-4,8-dibromoanthraquinone (20.0 g, 0.0324 mole), thiosalicyclic acid (11.55 g, 0.075 mole), potassium carbonate (10.35 g, 0.075 m), cupric chloride dihydrate (1.0 g) and DMF (175 mL) was heated at about 95°C for 4.0 hours and then drowned into acetone (400 mL). The solid which crystallized was collected by filtration, washed with acetone until the filtrate was no longer red. The dipotassium salt of the diacidic anthraquinone compound was dissolved by adding to water (500 mL) and stirring. The blue product which was precipitated by acidification with acetic acid was collected by filtration, washed with hot water and then dried in air (yield - 21.5 g). FDMS indicated the structure to be consistent with that given above in Example 10 for the starting diacidic anthraquinone compound.

Example 10b

A solution of 1,5-bis-(4-methylcyclohexanemethylamino)anthraquinone (65.0 g, 0.142 mole) dissolved in DMF (1.0 L) by stirring at about 55°C was treated with a solution of N-bromosuccinimide (50.5 g, 0.284 mole) in DMF (200 mL). After addition was completed, the bromination reaction was completed by heating at 55-60°C for 2.0 hours. Water (1.0 L) was added to precipitate the red product which was collected by filtration, washed with water and dried in air. After being reslurried in hot methanol and cooling, the product was collected by filtration, washed with a little methanol and air dried (yield - 84.0 g). FDMS indicated the structure to be that of the starting, dibrominated anthraquinone compound of Example 10a.

Example 10c

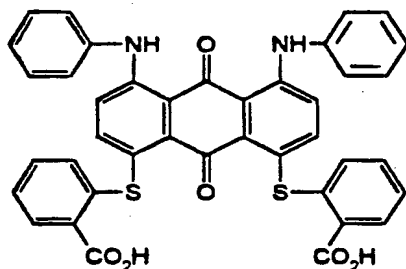
- 46 -

A mixture of 1,5-dichloroanthraquinone (48.0 g, 0.17 mole), 4-methyl-1-aminomethylcyclohexane (88.9 g, 0.70 mole), 2-ethoxyethanol (400 mL) was stirred and heated at reflux for 35.0 hours and the reaction mixture allowed to cool. The red product was precipitated by the addition of methanol and was collected by filtration, washed with methanol and dried in air (yield - 66.0 g). FDMS indicated the product to be the starting anthraquinone compound for Example 10b.

10

Example 11

A mixture of diacidic anthraquinone compound (0.69 g, 0.001 m) having the following structure



15

1,6-hexanediol, dimethanesulfonate (0.27 g, 0.001 mole), potassium carbonate (0.3 g) and DMF (5.0 mL) was heated with occasional stirring for 2.5 hours at about 95°C. The reaction mixture was drowned into methanol (100 mL) and the product collected by filtration, washed with methanol, water containing a little acetic acid and then finally with hot water and air dried (yield - 0.45 g). The blue polydye had an absorption maximum at 610 nm in DMF, a weight average molecular weight of 3,311 a number average

20
25

- 47 -

molecular weight of 1,272 and a polydispersity value of 2.63.

Example 11a

5 A mixture of 1,8-di-(2-carboxyphenylthio)-4,5-dinitroanthraquinone (4.00 g, 0.0066 mole), aniline (2.5 g) and nitrobenzene (30.0 mL) was heated at reflux with stirring for 5.0 hours. The reaction mixture was drowned
10 into hexane and the hexane decanted. The product was washed again by adding hexane, stirring and decanting. The crude product was slurried in acetone and heated to reflux and the blue product collected by filtration, washed with water and air dried (yield - 0.75 g). FDMS
15 indicated the product to be mostly 1,8-dianilino-4,5-di-(2-carboxyphenylthio)anthraquinone, the starting diacidic, anthraquinone compound for Example 11.

Example 11b

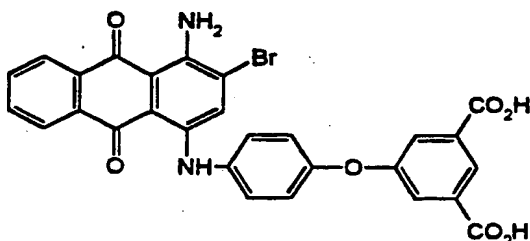
20 The potassium salt of thiosalicyclic acid (4.75 g, 0.03 mole) was made by addition to DMF (75 mL) and heating in the presence of potassium carbonate (8.70 g, 0.06 mole) for 2.0 hours at about 95°C. The cooled mixture was added
25 to a solution of 1,8-dichloro-4,5-dinitroanthraquinone (5.51 g, 0.015 mole) dissolved in DMF (150 mL) at about 0-5°C with stirring. The reaction mixture was allowed to warm to about 25°C with stirring continued for 2.0 hours and then poured into water. The product was obtained in
30 essentially quantitatively yield by slowly acidifying with 10% hydrochloric acid and was then collected by filtration, washed with water and dried in air. FDMS indicated the product to be mostly the starting anthraquinone compound used in Example 11a.

35

- 48 -

Example 12

A mixture of the diacidic anthraquinone compound (0.85 g. 0.0015 m) having the following structure



5

1,6-hexanediol, dimethanesulfonate (0.41 g, 0.0015 m), potassium carbonate (0.5 g) and DMF (5.0 mL) was heated at about 95°C for 2.0 hours with occasional stirring. The reaction mixture was drowned into methanol (100 mL) and the blue polydye was collected by filtration, washed with methanol, water containing a little acetic acid and finally hot water and then dried in air (yield - 0.62 g). GPC analysis indicated a weight average molecular weight of 20,020, a number average molecular weight of 2,313 and a polydispersity of 8.66. An absorption maximum was observed at 591 nm in the visible light absorption spectrum in DMF.

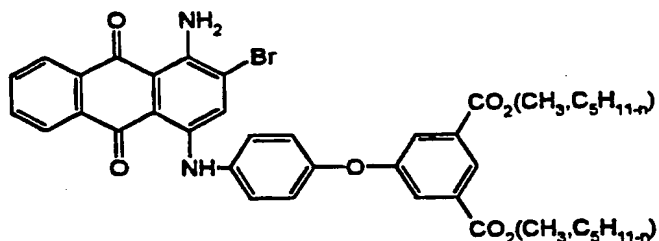
15

Example 12a

20

The anthraquinone diester compound (4.00 g) having the following structure

- 49 -



50% aqueous sodium hydroxide (2.40 g) and 2-ethoxyethanol (60 mL) were combined and heated with stirring at about 95°C for 0.5 hour. Hydrolysis of ester groups appeared to be complete by TLC (50:50 THF:cyclohexane). The reaction mixture was drowned into water (600 mL) and the blue solution acidified using acetic acid. The blue solid was collected by filtration washed with water and dried in air (yield - 3.80 g). FDMS indicated the structure to be mostly that of the starting diacidic anthraquinone compound in Example 12 plus a small amount of a violet compound probably produced by displacement of the bromine atom with the 2-(ethoxy)ethoxy group.

Example 12b

A mixture of 1-amino-2,4-dibromoanthraquinone (7.62 g, 0.02 mole), dimethyl 5(4-aminophenoxy)isophthalate (9.03 g, 0.03 mole), 1-pentanol (100 mL), potassium acetate 4.0 g), and cupric acetate (0.2 g) was heated at reflux for 4.0 hours and until all of the starting material had been used up as indicated by TLC analysis (20:80 THF:cyclohexane). Several blue components presumed to be a mixture of ester products produced by transesterification were observed. The reaction mixture was drowned into methanol (100 mL) and the product was collected by filtration, washed thoroughly with methanol to remove a red by-product and then washed with water and dried in air (yield - 7.81 g). FDMS indicated ions corresponding to the dimethylester,

- 50 -

monopentyl ester and dipentylester of the product - the structure of the starting material for Example 12a.

Example 12c

5 A mixture of dimethyl 5-(4-nitrophenoxy)isophthalate (30.0 g, 0.09 mole), isopropanol alcohol (350 mL) and ethanol wet Raney nickel catalyst (5.0 g) was hydrogenated at 90°C for 4.0 hours at 1500 psi hydrogen pressure in an
10 autoclave. Isopropanol (100 mL) was added to the reaction mixture from the autoclave and the solid product dissolved by heating. The Raney nickel was removed by hot filtration and the filtrate allowed to cool. The off-white solid was collected by filtration and dried in air
15 (yield - 17.8 g). FDMS indicated the product to be dimethyl 5-(4-aminophenoxy)isophthalate used in Example 12b.

Example 12d

20 A mixture of 1-chloro-4-nitrobenzene (47.1 g, 0.30 mole), dimethyl 5-hydroxyisophthalate (63.0 g, 0.30 mole), anhydrous potassium carbonate (41.4 g), potassium iodide (0.2 g) and DMF (200 mL) was heated at 120- 125°C for 1.5
25 hours, under a slow nitrogen sweep allowing some distillate to be removed (about 75 mL) via a Dean-Stark trap. Additional DMF (50 mL) was added back to the reaction mixture and heating continued for an additional 1.5 hours while an additional amount of distillate (25 mL)
30 was allowed to collect in the Dean-Stark trap. The reaction mixture was allowed to cool to about 45°C. A heavy slurry of pale yellow product resulted which was diluted further by the addition of an ice-water mixture (350 g) with good stirring. Filtration followed by
35 washing with water and drying in air gave the pale yellow dimethyl 5-(4-nitrophenoxy)isophthalate (90.7 g)

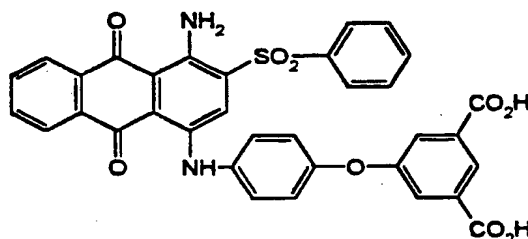
- 51 -

(structure supported by FDMS) which was used in Example 12c.

Example 13

5

A mixture of the diacidic anthraquinone compound (1.26 g, 0.002 mole) having the following structure



- 10 1,6-hexandiol, dimethanesulfonate (0.58 g, 0.002 mole), potassium carbonate (0.5 g) and DMF (6.0 mL) was heated at 90-95°C for 2.0 hours with occasional stirring. The reaction mixture was drowned into methanol (100 mL) and the dark blue-green polydye was collected by filtration,
- 15 washed with methanol, water containing a little acetic acid and finally with water and then dried in air (yield 1.13 g). GPC analysis indicated a weight average molecular weight of 14,776, a number average molecular weight of 2,514 and a polydispersity of 5.88. An
- 20 absorption maximum was observed at 620 nm in the visible light absorption spectrum in DMF.

Example 13a

- 25 A portion (1.72 g, 0.003 mole) of the bromoanthraquinone product of Example 12a, benzenesulfinic acid, Na salt (0.98 g, 0.006 mole), potassium carbonate (1.38 g) and DMF (25 mL) were mixed and the reaction mixture heated with stirring at 90-95°C for 1.0 hour. A bathochromic shift in

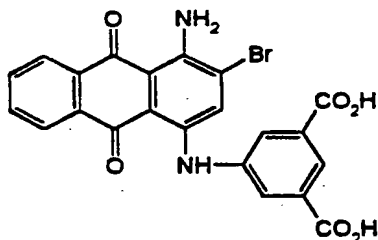
- 52 -

color was observed as the 2-bromo substituent was replaced by the 2-phenylsulfonyl group on the anthraquinone nucleus. The greenish-blue solution was drowned into acetone (100 mL) and the solid material was collected by
5 filtration and washed with acetone until the filtrate was pale blue. The acetone-wet solid was added with stirring to water (200 mL) and the mixture acidified with acetic acid. After being heated to about 75°C, the reaction mixture was filtered and the dark blue solid was washed
10 with hot water and dried in air (yield - 1.50 g). FDMS indicated the structure to be that of the starting diacidic anthraquinone compound used in Example 13.

Example 14

15

A mixture of the diacidic anthraquinone compound (1.45 g, 0.003 mole) having the structure



20 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at about 95°C for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the blue polydye was collected by filtration and washed with methanol, water
25 containing a little acetic acid and finally hot water and dried in air (yield - 1.10 g). GPC analysis indicated a weight average molecular weight of 3,727, a number average weight of 1,031 and a polydispersity of 3.61. Absorption

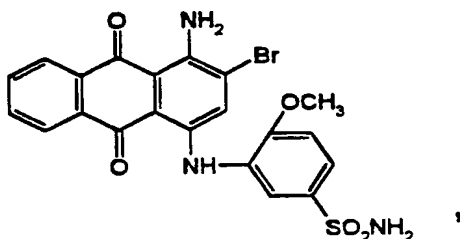
- 53 -

maxima were observed at 623 nm and 585 nm in the visible light absorption spectrum in DMF.

Example 15

5

A mixture of the diacidic anthraquinone compound (1.50 g, 0.003 mole) having the following structure



10 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated with occasional stirring at about 95°C for 2.0 hours. The reaction mixture was then drowned into methanol (100 mL) and the blue polydye was collected by filtration, washed
15 with methanol, water containing a little acetic acid, and hot water and then dried in air (yield- 0.90 g). An absorption maximum at 591 nm was observed in the visible light absorption spectrum in DMF.

20 Example 15a

To DMF (40mL) was added 1-amino-2-Br-4-(5-chlorosulfonyl-2-methoxyanilino) anthraquinone (4.0 g) with stirring. When solution appeared to be complete, conc. ammonium
25 hydroxide (4.0 g) was added and stirring was continued at ambient temperature for 30 minutes. TLC using 50:50 THF:cyclohexane indicated complete reaction of the sulfonyl chloride compound to produce the desired sulfonamide. The reaction mixture was drowned into water

- 54 -

and the blue product was collected by filtration, washed with water and air dried (yield- 3.8 g). FDMS indicated the structure to be that of the starting compound for Example 15.

5

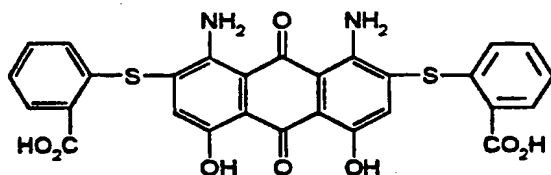
Example 15b

To chlorosulfonic acid (100 mL) was added 1-amino-4-o-anisidino-2-bromoanthraquinone (10.0 g, 0.0236 mole)
10 portionwise with good stirring at 25-30°C. After addition was completed, the reaction mixture was stirred at room temperature for 1.0 hour. The reaction mixture was added in a fine stream to cold isopropanol (800 mL) with stirring. The blue product was collected by vacuum
15 filtration on a sintered glass funnel, washed with isopropanol and dried in air (yield- 10.3 g) and used without further purification in Example 15a.

Example 16

20

A mixture of the diacidic anthraquinone compound (0.58 g, 0.001 m) having the following structure



1,2-ethanediol, dimethanesulfonate (0.22 g, 0.001 m),
25 potassium carbonate (0.3 g) and DMF (5.0 mL) was heated at 95°C for 2.5 hours. The reaction mixture was drowned into methanol (100 mL) and the greenish-blue polydye was collected by filtration, washed with methanol, water containing a little acetic acid and water and then air
30 dried (yield - 0.33 g). GPC analysis indicated a weight

- 55 -

average molecular weight of 4,144 a number average molecular weight of 1,643 and a polydispersity of 2.52. An absorption maximum at 629 nm was observed in the visible light absorption spectrum in DMF.

5

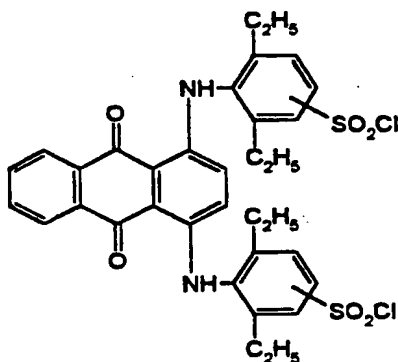
Example 16a

A mixture of 1,8-diamino-2,7-dibromo-4,5-dihydroxyanthraquinone (2.19 g, 0.005 mole),
10 thiosalicyclic acid (1.60 g, 0.104 mole), potassium carbonate (1.5 g) and DMF (25.0 mL) was heated at 95-100°C for 6.0 hours. A bathochromic shift in color occurred as the two bromine atoms were replaced by the 2-carboxyphenylthio groups. The reaction mixture was
15 drowned into methanol and the solid product was collected by filtration and washed with methanol. The product was dissolved in water (100 mL) and the diacidic anthraquinone which precipitated by addition of acetic acid was
20 collected by filtration, washed with water and dried in air (yield - 0.86 g). FDMS indicated the product to be that used as starting material for Example 16.

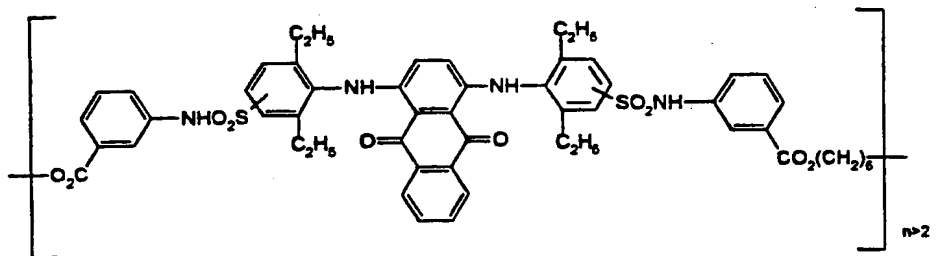
Example 17

25 The anthraquinone disulfonyl chloride compound (3.50 g, 0.005 mole) having the following structure

- 56 -



(prepared according to the procedure of U. S. Patent 5,453,482, Example 2), m-aminobenzoic acid (1.37 g, 0.10 mole), potassium carbonate (2.80 g) and DMF (30 mL) were mixed and the reaction mixture heated at 90-95°C for 30 minutes. TLC (50:50 THF:cyclohexane) indicated complete reaction of the disulfonyl chloride to produce the disulfonamide derivative. To the reaction mixture were added 1,6-hexanediol, dimethanesulfonate (1.38 g, 0.005 m), potassium carbonate (1.38 g) and heating and stirring were continued for 2.0 hours at 90-95°C. The reaction mixture was drowned into water and acidified with acetic acid. The bright blue polydye was collected by filtration, washed with water and then air dried (yield - 2.07 g) and is believed to have the following repeat unit:

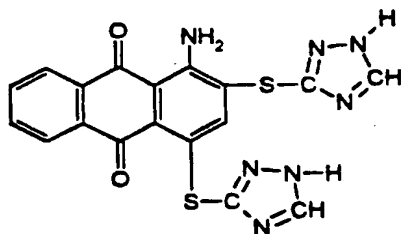


- 57 -

GPC analysis indicated a weight average molecular weight of 5,252, a number average molecular weight of 2,179 and a polydispersity of 2.41. Absorption maxima at 583 nm and 628 nm were observed in the visible light absorption spectrum in DMF.

Example 18

A mixture of the diacidic anthraquinone compound (4.21 g, 0.01 mole) having the following structure



1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole), potassium carbonate (2.68 g, 0.02 mole) and DMF (50 mL) was heated and stirred at 90-95°C for 1.5 hours. The reaction mixture was drowned into water (400 mL) and acidified with stirring and by adding acetic acid. After being heated to about 50°C, the mixture was filtered and the red polydye washed well with water and dried in air (yield - 4.47 g). GPC analysis showed the polydye to have a weight average molecular weight of 1,603, a number average molecular weight of 922 and a polydispersity of 1.74. An absorption maximum at 524 nm was observed in the visible light absorption spectrum in DMF.

Example 18a

A mixture of 1-amino-2,4-dibromoanthraquinone (11.43 g, 0.03 mole), 3-mercapto-1(H)-1,2,4-triazole (9.09 g, 0.09

- 58 -

mole), potassium carbonate (11.52 g, 0.09 mole) and DMF (150 mL) was heated at about 95°C with stirring for 1.0 hour. The reaction mixture was drowned into water (500 mL) with stirring and acidified with acetic acid and the
5 red product collected by filtration, washed with water and dried in air (yield - 12.64 g). FDMS indicated the product to be the diacidic anthraquinone compound used in Example 18.

10 Example 19

A mixture of 1,5-bis-(4-hydroxyphenylthio)anthraquinone (4.56 g, 0.01 mole), 1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole), potassium carbonate (3.0 g) and DMF
15 (50 mL) was heated and stirred at about 95°C for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the yellow polydye was collected by filtration and washed with methanol. The methanol-wet cake was reslurried in water (500 mL) and acidified and
20 the polydye then collected by filtration, washed with water and dried in air (yield - 4.25 g). GPC analysis indicated the polydye to have a weight average molecular weight of 1,901, a number average molecular weight of 1,588 and a polydispersity of 1.20. An absorption maximum
25 at 461 nm was observed in the visible light absorption spectrum in DMF.

Example 19a

30 A mixture of 1,5-dichloroanthraquinone (5.54 g, 0.02 mole), 4-hydroxybenzenethiol (6.30 g, 0.05 mole), potassium carbonate (6.90 g, 0.05 mole) and DMF (100 mL) was heated at about 95°C for 5.0 hours. The reaction mixture was drowned into water (400 mL) and the yellow
35 product was collected by filtration, washed with water and dried in air (yield - 9.0 g). The solid was added to

- 59 -

acetic acid (150 mL) and the mixture heated to boiling. After being allowed to cool, the yellow solid was collected by filtration, washed with acetic acid and dried in air (yield - 6.75 g). FDMS confirmed that the product
5 was the 1,5-bis(4-hydroxyphenylthio)anthraquinone used in Example 19.

Example 20

10 A mixture of 1,4-bis-(2-carboxyphenylthio)anthraquinone (1.53 g, 0.003 m), 1,2-ethanediol, dimethanesulfonate (0.66 g, 0.003 mole), potassium carbonate (0.75 g) and DMF (8.0 mL) was heated at about 95°C with occasional stirring for 2.0 hours. The reaction mixture was then drowned into
15 methanol (100 mL) and the dark orange polydye was collected by filtration, washed with water containing some acetic acid then with hot water and dried in air (yield - 0.50 g). GPC analysis indicated a weight average molecular weight of 8,686, a number average molecular
20 weight of 1,356 and a polydispersity of 6.41.

Example 20a

A mixture of 1,4-dichloroanthraquinone (2.77 g, 0.01
25 mole), thiosalicylic acid (3.85 g, 0.025 m), potassium carbonate (3.45 g, 0.025 m), cupric chloride dihydrate (0.1 g) and DMF (50 mL) was heated at 95-100°C with stirring for 4.0 hours. The reaction mixture was drowned into acetone and the solid was collected by filtration and
30 washed with acetone. The resulting potassium salt of the product was dissolved by stirring in water (200 mL). The red solution was neutralized to give the orange product which was collect by filtration, washed with water and dried in air (yield - 4.58 g). FDMS indicated the
35 structure to be that of the starting material for Example

- 60 -

20. An absorption maximum at 501 nm was observed in the visible light absorption spectrum.

Example 21

5

A mixture of 1,8-bis-(2-carboxyphenylthio)-4,5-bis-(p-tolylthio)anthraquinone (1.51 g, 0.002 mole), 1,4-butanediol, dimethanesulfonate (0.49 g, 0.002 mole), potassium carbonate (0.60 g) and DMF (8.0 mL) was heated at 10 90-95°C with occasional stirring for 2.5 hours. The reaction mixture was drowned into methanol (100 mL) and the red polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield - 1.1 g). GPC analysis indicated a 15 weight average molecular weight of 2,157, a number average molecular weight of 1,111 and a polydispersity of 1.94. An absorption maximum was observed at 529 nm in the visible light absorption spectrum in DMF.

20 Example 21a

A mixture of thiosalicyclic acid (4.75 g, 0.03 mole), potassium carbonate (8.70 g, 0.06 mole) and DMF (75 mL) was heated at about 100°C for 1.0 hour and the reaction 25 mixture, which was allowed to cool, was added at 0-5°C to a solution of 1,8-dichloro-4,5-dinitroanthraquinone (5.51 g, 0.015 mole) dissolved in DMF (150 mL) with good stirring. Cooling was removed and the temperature of the reaction mixture allowed to come to ambient temperature 30 and the mixture was stirred for about 3.0 hours. A solution of p-thiocresol (3.73 g, 0.03 mole) dissolved in DMF (80 mL) was added to the reaction mixture with stirring and the temperature raised to about 100°C and held for 2.0 hours. After allowing to cool, the reacting 35 mixture was drowned into water (300 mL) and the mixture gradually acidified by the addition of 10% aqueous

- 61 -

hydrochloric acid. The red solid product was collected by filtration, washed with water and dried in air (yield - 11.28 g). FDMS analysis indicated that the product consisted mostly of the starting material for Example 21.

5

Example 22

A mixture of 1,5-bis(2-carboxyphenylthio)anthraquinone (1.54 g, 0.003 mole), 1,5-bis(2-carboxyphenylthio)-4,8-bis(isobutylamino)anthraquinone (1.31 g, 0.002 mole) (product of Example 2a), 1,2-ethandiol, dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.0 g) and DMF (10 mL) was heated at 90-95°C with occasional stirring for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the green polydye was washed with methanol, water containing acetic acid, hot water and then dried in air (yield - 1.30 g). GPC analysis indicated a weight average molecular weight of 1,839, a number average molecular weight of 1,040 and a polydispersity of 1.77. Absorption maxima were observed in the visible light absorption spectrum in DMF at 448, 603, and 645 nm.

20

Example 23

A mixture of 1,5-bis(2-carboxyphenylthio)anthraquinone (1.28 g, 0.0025 mole), 1,4-cyclohexanedimethanol, dimethanesulfonate (1.75 g, 0.0025 mole), potassium carbonate (0.82 g) and DMF (7.5 mL) was heated at about 95°C with occasional stirring for 3.0 hours. The reaction mixture was drowned into methanol (100 mL) and the yellow polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield - 0.31 g). GPC analysis indicated a weight average molecular weight of 1,158, a number average molecular weight of 1,008 and a polydispersity of 1.15.

30

35

- 62 -

Example 24

Example 23 was repeated except that the disulfonate used was 1,3-propanediol, 2,2-dimethyl, dimethanesulfonate (0.65 g, 0.0025 mole) to give the yellow polydye (yield - 0.76 g) which had a weight average molecular weight of 1,056, a number average molecular weight of 979 and a polydispersity of 1.08 by GPC analysis.

10 Example 25

Example 23 was repeated except that 1,6-hexanediol, dimethanesulfonate (0.68 g, 0.0025 mole) was used as the disulfonate to give the yellow polydye (yield - 1.16 g) which had a weight average molecular weight of 1,827, a number average molecular weight of 961 and a polydispersity of 1.90 by GPC analysis.

Example 26

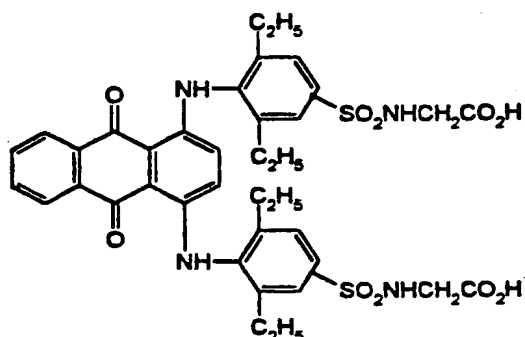
20

Example 23 was repeated except that 1,2-ethanediol, bis(4-methylbenzenesulfonate (0.82 g, 0.0025 mole) was used as the disulfonate to yield the yellow polydye (yield - 0.41 g) which had a weight average molecular weight of 2,442, a number average molecular weight of 1,885 and a polydispersity of 1.29 by GPC analysis.

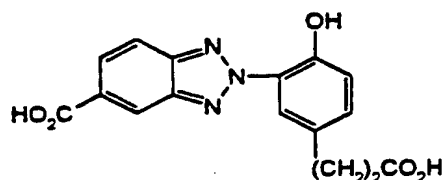
Example 27

30 A mixture of the acidic anthraquinone compound (2.02 g, 0.0027 mole) having the structure

- 63 -



the acidic UV light absorbing compound (0.29 g, 9×10^{-4} mole) having the structure

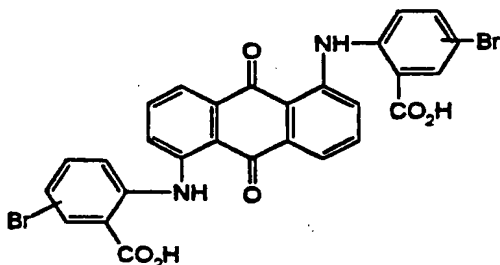


- 5 1,2-ethanediol, dimethanesulfonate (0.78 g, 0.0036 mole), potassium carbonate (1.0 g) and DMF (25 mL) was heated and stirred at 90-95°C for 2.0 hours. The cooled reaction mixture was drowned into water (200 mL) and made slightly
- 10 acidic by the addition of acetic acid with stirring. The polymeric product was collected by filtration, washed well with water and dried in air (yield - 2.00 g). GPC analysis indicated a weight average molecular average of 5,642, a
- 15 number average molecular weight of 1,720 and a polydispersity of 3.28.

Example 28

- A mixture of the diacidic anthraquinone compound (1.27 g, 20 0.002 mole) having the structure

- 64 -



1,2-ethanediol, dimethanesulfonate (0.44 g, 0.002 mole), potassium carbonate (0.75 g) and DMF (8.0 mL) was heated at 90-95°C with occasional stirring for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the dark red polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield - 1.23 g). GPC analysis indicated a weight average molecular weight of 1,545, a number average molecular weight of 1,213 and a polydispersity of 1.27.

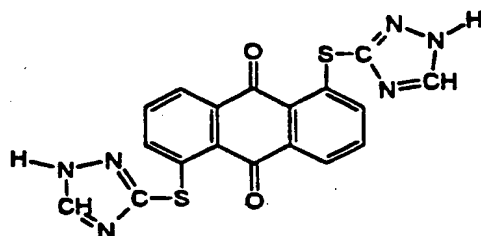
Example 28a

To a mixture of 1,5-bis(2-carboxyanilino)anthraquinone (9.57 g, 0.02 mole) in DMF (250 mL) was added portionwise N-bromosuccinimide (7.12 g, 0.04 mole) with stirring at room temperature. The reaction mixture was then heated at about 60°C for 1.5 hours and allowed to cool. Water was added dropwise to precipitate the product, which was collected by filtration, washed with water and dried in air (yield - 11.17 g). FDMS indicated the structure of the product to be that of the starting anthraquinone compound in Example 28.

Example 29

A mixture of the diacidic anthraquinone compound (4.06 g, 0.01 mole) having the structure

- 65 -



1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole),
potassium carbonate (2.76 g) and DMF (150 mL) was heated
5 at about 100°C for 3.0 hours. The reaction mixture was
drowned into water, acidified with acetic acid and the
yellow polydye was collected by filtration, washed with
water and dried in air. GPC analysis indicated a weight
average molecular weight of 5,333, a number average
10 molecular weight of 2,441, and a polydispersity of 2.18.

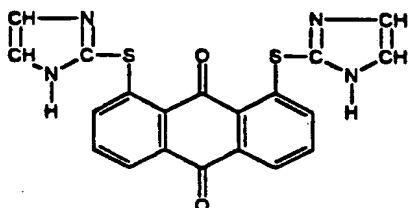
Example 29a

A mixture of 1,5-dichloroanthraquinone (6.93 g, 0.025
15 mole), 3-mercapto-1(H)-1,2,4-triazole (5.56 g, 0.055
mole), potassium carbonate (6.91 g, 0.05 mole) and DMF
(100 mL) was heated and stirred at about 95°C for 5.0
hours. The mixture was drowned into water and the yellow
product was collected by filtration, washed with water and
20 air dried. The cake was reslurried in hot isopropanol and
the product collected by filtration, washed with
isopropanol and dried in air (yield 8.62 g). FDMS
indicated the product to be 1,5-bis[1(H)-1,2,4-triazol-3-
ylthio]anthraquinone used as the diacidic anthraquinone
25 starting material in Example 29.

Example 30

- 66 -

A mixture of diacidic anthraquinone compound (1.01 g, 0.0025 mole) having the structure



5 1,2-ethanediol, dimethanesulfonate (0.55 g, 0.0025 mole), potassium carbonate (0.75 g) and DMF (10 mL) was heated at about 95°C for 3.0 hours. The reaction mixture was then drowned into methanol (100 mL) and the yellow polydye was collected by filtration, water containing acetic acid, hot
10 water and then air dried (yield - 0.35 g). GPC analysis indicated a weight average molecular weight of 2,478, a number average molecular weight of 742 and a polydispersity of 3.34. An absorption maximum was observed in the visible light absorption spectrum at 425
15 nm in DMF.

Example 30a

A mixture of 1,8-dichloroanthraquinone (6.93 g, 0.025
20 mole), 2-mercaptoimidazole (5.01 g, 0.05 mole), potassium carbonate (6.91 g) and DMF (60 mL) was heated and stirred at about 95°C for 8.0 hours. The reaction mixture was drowned into water and acidified using acetic acid. The yellow product was collected by filtration, washed with
25 water and dried in air. FDMS indicated the product to be the 1,8-bis(imidazol-2-ylthio) anthraquinone diacidic compound used as the starting material in Example 30.

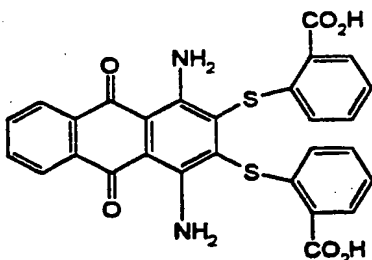
Example 31

- 67 -

A mixture of 1,5-bis[1(H)-1,2,4-triazol-3ylthio] anthraquinone (1.80 g, 0.00443 mole) (product of Example 29a), 1,4-dibromobutane (0.96 g, 0.00444 mole),
5 tributylamine (1.64 g, 0.00885 mole), and N-methyl-2-pyrrolidinone (30 mL) was heated at 8.0 hours at about 130°C with stirring. The reaction mixture was drowned into acetone (150 mL) and the yellow polydye was collected by filtration, washed with acetone until filtrate was
10 essentially clear and dried in air. GPC analysis indicated a weight average molecular weight of 5,022, a number average molecular weight of 3,220 and a polydispersity of 1.56.

15 Example 32

A mixture of the diacidic anthraquinone compound (1.63 g, 0.003 mole) having the structure



20

1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at about 95°C with occasional stirring for 2.0 hours. The mixture was drowned into methanol (100 mL) and the dark
25 blue polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 0.92 g). Absorption maxima at 602

- 68 -

and 644 nm were observed in the visible light absorption spectrum in DMF. GPC analysis indicated a number average molecular weight of 1,860.

5 Example 32a

A mixture of 1,4-diamino-2,3-dichloroanthraquinone (12.24 g, 0.04 mole), thiosalicylic acid (15.4 g, 0.10 mole), potassium carbonate (13.8 g, 0.10 mole) and DMF (150 mL) was heated at about 95°C with stirring for 2.0 hours. A bathochromic shift in color from violet to blue was observed as the reaction progressed. The reaction mixture was drowned into acetone (500 mL) and the solid product was collected by filtration and washed well with acetone. The acetone-wet cake was added to water (600 mL) and the mixture acidified with acetic acid to precipitate the free acid compound, which was collected by filtration, washed with water and dried in air (yield - 21.4 g). FDMS indicated the product to be the 1,4-diamino-2,3-bis(2-carboxyphenylthio) anthraquinone used in Example 32.

Example 33

A mixture of 1,5-bis(2-carboxyphenylthio) anthraquinone (1.02 g, 0.002 mole), terephthalic acid (1.00 g, 0.006 mole), potassium carbonate (1.38 g), 1,2-ethanediol, dimethanesulfonate (1.74 g, 0.008 mole) and DMF (10 mL) was heated at about 95°C with occasional stirring for 2.0 hours. The mixture was then drowned into methanol (100 mL) and the yellow polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 1.88 g). GPC analysis indicated a weight average molecular weight of 794, a number average molecular weight of 713 and a polydispersity of 1.11.

- 69 -

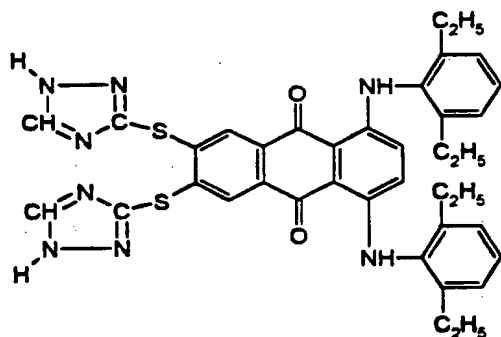
Example 34

Example 33 was repeated using 1,5-bis(2-carboxyphenylthio) anthraquinone (1.02 g, 0.002 mole) and terephthalic acid
5 (0.33 g, 0.002 mole), 1,2-ethanediol, dimethanesulfonate (0.87 g, 0.004 mole) and potassium carbonate (0.87 g) to yield the yellow polydye (0.90 g). GPC analysis indicated a weight average molecular weight of 875, a number average molecular weight of 811, and a polydispersity of 1.08.

10

Example 35

A mixture of the diacidic anthraquinone compound (2.00 g, 0.00285 mole) having the following structure (Preparation
15 5 of IR Docket 70351):



1,2-ethanediol, dimethanesulfonate (0.63 g, 0.00289 mole), potassium carbonate (0.80 g) and DMF (25 mL) was heated at
20 95°C for 4.0 hours with stirring. The reaction mixture was drowned into methanol (100 mL) and the greenish-blue polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 1.01 g). GPC indicated a weight average
25 molecular weight of 6,720, a number average molecular

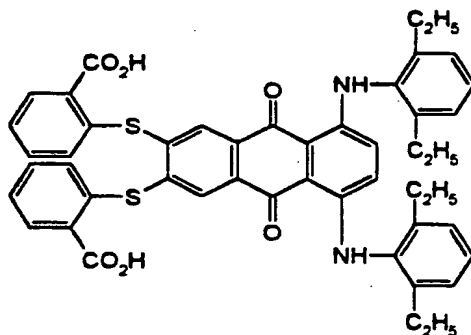
- 70 -

weight of 2,211 and a polydispersity of 3.04. Absorption maxima were observed at 599 and 647 nm in the visible absorption spectrum in DMF.

5 Example 36

A mixture of the diacidic anthraquinone compound (0.41 g, 0.508 mmole) having the following structure (Preparation 4 in IR Docket 70351):

10



1,2-ethanediol, dimethanesulfonate (0.11 g, 0.504 mmole), potassium carbonate (0.14 g) and DMF (5.0 mL) was heated with occasional stirring or about 95°C for 3.0 hours. The reaction mixture was drowned into methanol (50 mL) and the greenish-blue polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield 0.15 g). Absorption maxima were observed at 599 and 645 nm in the visible light absorption spectrum in DMF.

Example 37-66

Colored EASTAR® copolyester 6763 film was produced by melt blending the polydyes of Examples 7-36 and extruding

- 71 -

according to the following procedure to produce Examples 37-66 (Table 1).

5 EASTAR® PETG polyester 6763, a poly(ethylene-1,4-cyclohexanedimethylene) terephthalate (Eastman Chemical Company) (300 g of previously dried pellets) was dry blended with the anthraquinone polydye composition (0.12 g). The blend was extruded with a C. W. Brabender $\frac{3}{4}$ in. extruder, equipped with a mixing screw, at 250°C into a
10 water bath and the extrudate pelletized.

The pellets were redried at 70°C for 17 hrs. at a pressure of about 1-5 torr. A portion (1.40 g) of the dried pellets was pressed into a 18-20 mil film at 250°C using a
15 2-inch diameter circular mold in a Pasadena Hydraulic, Inc. press using 12,000 pounds ram force (4 inch ram). The transparent films contained about 300 ppm of the polydyes and each showed excellent color development to produce the colors indicated in Table 1.

20

Example 67

A mixture of 1,4-bis(2-carboxyphenylthio)anthraquinone (15.4 g, 0.03 mole) (prepared as in Example 20a), 1,5-
25 bis(2-carboxyphenylthio)-4,8-bis(isobutylamino)anthraquinone (6.55 g, 0.01 mole) (Example 2a), 1,2-ethanediol, dimethanesulfonate (8.72 g, 0.04 mole), potassium carbonate (8.0 g) and DMF (100 mL) was stirred and heated at about 95°C for 2.0 hours with
30 occasional stirring. The reaction mixture was drowned into methanol (500 mL) and the black polydye was collected by filtration, washed with water containing acetic acid, hot water and dried in air (yield - 9.5 g). GPC analysis indicated a weight average molecular weight of 7,512, a
35 number average molecular weight of 1,700 and a polydispersity of 4.42.

- 72 -

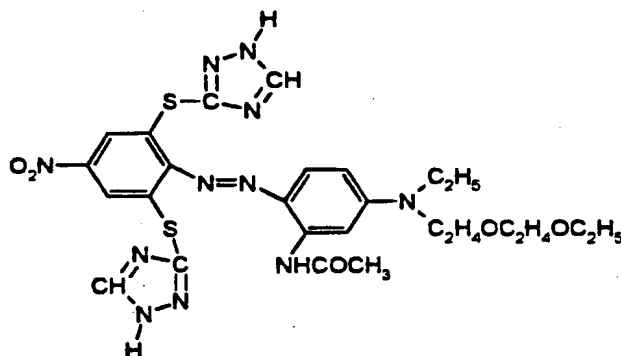
Example 68

5 EASTAR® PETG copolyester 6763 (291 g of previously dried pellets) was dry blended with the black polydye of Example 67 (9.0 g) and the blend extruded and a portion of the resulting pellets was pressed into a black film containing approximately 3.0% by weight of polydye by using the procedure described in Example 4.

10

Example 69

A mixture of the diacidic azo compound (3.20 g, 0.005 mole) having the structure



15

1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.5 g) and DMF (25 mL) was heated and stirred at about 95°C for 3.0 hours. The reaction mixture was drowned into methanol and the violet polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 1.60 g). GPC analysis indicated a weight average molecular weight (M_w) of 6,403, a number average molecular weight (M_n) of 3,700 and a polydispersity (M_w/M_n) of 1.73.

20

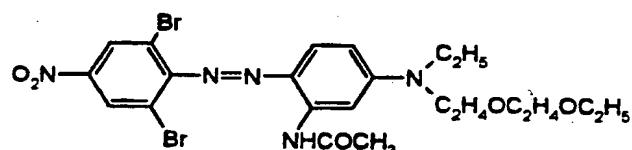
- 73 -

In the visible light absorption spectrum in DMF an absorption maximum was observed at 556 nm.

Example 69a

5

A mixture of the dibromoazobenzene dye (6.01 g, 0.010 mole) having the structure

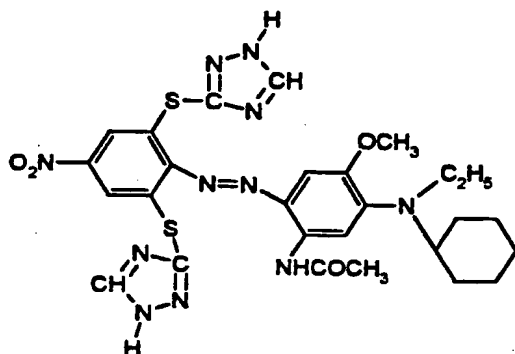


- 3-mercapto-1(H)1,2,4-triazole (2.2 g, 0.022 mole),
 10 potassium carbonate (3.45 g, 0.025 mole) and DMF (100 mL)
 was stirred and heated at about 95°C for 2.0 hours. TLC
 (75 parts THF: 25 parts cyclohexane) showed incomplete
 reaction. An additional quantity (1.01 g, 0.01 m) 3-
 15 mercapto-1(H)-1,2,4-triazole was added and heating and
 stirring were continued for 2.0 additional hours. TLC
 indicated essentially complete reaction to produce the
 violet product. The reaction mixture was drowned into
 water (400 mL) and the mixture was acidified by addition
 of acetic acid, heated to about 40°C and filtered. The
 20 product was washed with warm water and dried in air (yield
 - 5.60 g). FDMS indicated the product to have the
 structure of the diacidic azobenzene compound used in
 Example 69.

25 Example 70

A mixture of the diacidic azo compound (1.59 g, 0.0025 mole) having the structure

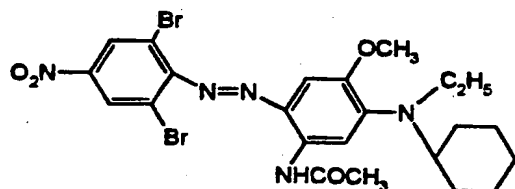
- 74 -



- 1,2-ethanediol, dimethanesulfonate (0.55 g, 0.0025 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at 95°C with occasional stirring for 3.0 hours. The reaction mixture was drowned into methanol (100 mL) and the blue polydye product was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 1.06 g). GPC analysis indicated a Mw of 5,497, a Mn of 2,648 and a Mw/Mn of 2.08. An absorption maximum was observed at 605 nm in DMF in the visible light absorption spectrum.

Example 70a

- A mixture of the dibromo azobenzene dye (2.38 g, 0.004 mole) having the structure

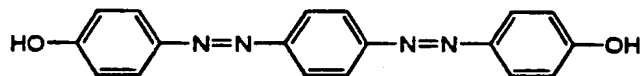


- 75 -

3-mercapto-1(H)-1,2,4-triazole (1.21 g, 0.012 mole), potassium carbonate (1.65 g, 0.012 mole) and DMF (25 mL) was heated and stirred for 1.0 hour. TLC (50 parts THF:50 parts cyclohexane) showed complete reaction to produce the product. The reaction mixture was drowned into water (100 mL) and the mixture acidified with acetic acid. The dark blue product was collected by filtration, washed with water and dried in air (yield - 2.55g). FDMS indicated the product to have the structure of the diacidic azobenzene compound used in Example 70.

Example 71

A mixture of the diacidic disazo compound (1.59 g, 0.005 mole) having the structure

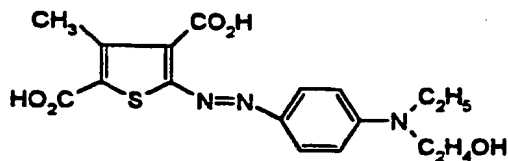


1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.5 g), DMF (10 mL) was heated and stirred at about 95°C for 3.0 hours. The reaction mixture was drowned into methanol (100 mL) and the dark brown polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield - 0.66 g). GPC analysis indicated a Mw of 4,926, a Mw of 1,574 and a Mw/Mn of 3.13.

Example 72

A mixture of the diacidic azo compound (1.88 g, 0.005 mole) having the structure

- 76 -



1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.5 g) and DMF (20 mL) was heated at about 95°C with stirring for 3.0 hours. The reaction mixture was drowned in methanol (100 mL) and the red polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 1.35 g). GPC analysis indicated a Mw of 6,888, a Mn of 2,127 and a Mw/Mn of 3.24. An absorption maximum was observed at 527 nm in the visible light absorption spectrum in DMF.

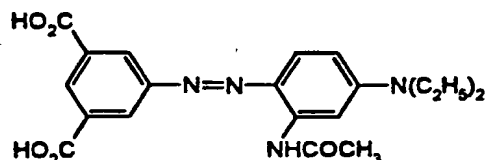
Example 72a

To a stirred mixture of the azo compound (4.05 g, 0.01 mole) [4-(3',5'-dicarbomethoxy-4'-methylthiophene-2-ylazo)-N-ethyl-N(2-hydroxyethyl)aniline] and 2-ethoxyethanol (50 mL) at room temperature was added aqueous 50% NaOH solution (3.75 g). After being heated at about 95°C for 1.0 hour, the reaction product was drowned into acetone (300 mL). The disodium salt of the diacidic azo dye was collected by filtration washed with acetone and then quickly dissolved in water (200 mL). Acidification with acetic acid precipitated the free diacid dye, which was collected by filtration, washed with water and dried in air (yield - 2.35 g). FDMS indicated the product to have the structure of the diacidic azo compound used in Example 72.

Example 73

- 77 -

A mixture of the diacidic azobenzene compound (1.19 g, 0.003 mole) having the structure



5 1,2-ethanediol, dimethanesulfonate (0.66 g, 0.003 mole), potassium carbonate (0.75 g), and DMF (8.0 mL) was stirred occasionally and heated at about 95°C for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the orange polydye was collected by filtration, washed
10 with methanol, water containing acetic acid, hot water and dried in air (yield - 0.65 g). GPC analysis showed a Mw of 3,015, a Mn of 2,128 and a Mw/Mn of 1.42. An absorption maximum was observed in the visible light absorption at 479 nm in DMF.

15

Example 73a

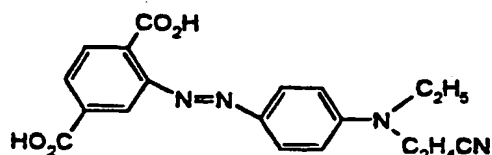
To a mixture of 3-acetamido-4-(3',5'-dicarbomethoxyphenylazo)-N,N-diethylaniline (1.7 g, 0.004
20 mole) in 2-ethoxyethanol (20 mL) was added aqueous 50% NaOH (1.6 g). The reaction mixture was heated with stirring of 95°C for 10 minutes and then drowned into water (100 mL). The solution was acidified with acetic acid to precipitate the diacid dye which was collected by
25 filtration, washed with water and dried in air (yield - 1.6 g). FDMS indicated the structure to be that of the starting diacid azobenzene compound in Example 73.

Example 74

30

- 78 -

A mixture of the diacidic azobenzene compound (1.10 g, 0.003 mole) having the structure



- 5 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.45 g) and DMF (8.0 mL) was heated at 95°C with occasional stirring for 2.0 hours. The reaction mixture was drowned into methanol (100 mL). A slightly sticky yellow product resulted. The methanol was removed by decantation and the product dissolved in DMF (10 mL) by heating and stirring. Water (100 mL) was added and the mixture acidified by addition of acetic acid. The solid yellow polydye was collected by filtration, washed with water and dried in air (yield - 0.47 g). GPC analysis indicated a Mw of 9,314, a Mn of 3,208 and a Mw/Mn of 2.90. An absorption maximum at 428 nm was observed in the visible light absorption spectrum in DMF.

Example 74a

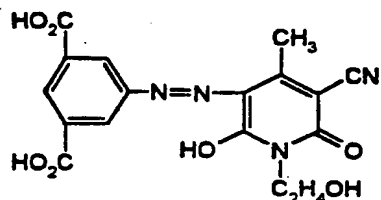
- 20 To a mixture of 4-(2',5'-dicarbomethoxyphenylazo)-N-(2-cyanoethyl)-N-ethylaniline (1.97 g, 0.005 mole) in 2-ethoxyethanol (20 mL) was added aqueous 50% NaOH (1.90 g). The reaction solution was heated at 95°C for 15 minutes and then drowned into water (200 mL). The solution was acidified and the yellow dye which precipitated was collected by filtration, washed with water and dried in air (yield - 1.75 g). FDMS indicated the structure to be that of the starting diacid azobenzene dye of Example 74.

30

Example 75

- 79 -

A mixture of diacidic azo compound (38.6 g, 0.10 mole) having the structure



5

1,6-hexanediol, dimethanesulfonate (27.4 g, 0.10 mole), potassium carbonate (27.6 g, 0.20 mole), and DMF (350 mL) was heated at 95-100°C for 2.0 hours. The reaction mixture was drowned into a solution of acetic acid (70.0 mL) in water (1700 mL) with good stirring. After stirring for about 15 minutes, the yellow polydye was collected by filtration, washed with hot water and dried in air (yield - 42.6 g). An absorption maximum at 422 nm was observed in the visible light absorption spectrum in DMF.

15

Example 75a

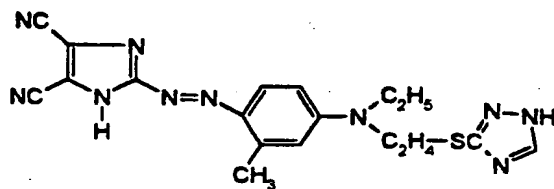
To a mixture of the diester dye (41.4 g, 0.10 mole) [3-cyano-5-(3',5'-dicarbomethoxyphenylazo)-6-hydroxy-N-(2-hydroxyethyl)-4-methyl-2-pyridone] in 2-ethoxyethanol (400 mL) was added aqueous 50% NaOH (40.0 g) and the reaction mixture was heated at 75-80°C for about 30 minutes. Acetone (200 mL) was added to the slightly cooled reaction mixture. The yellow solid was collected by filtration, washed with acetone and then reslurried in warm water (750 mL). After acidification using conc. HCl (20 mL), the yellow diacid dye was collected by filtration, washed with hot water and dried in air (yield- 36.0 g). FDMS indicated the structure to be that of the starting diacid azo compound of Example 75.

30

- 80 -

Example 76

A mixture of the diacidic azo compound (2.03 g, 0.005 mole) having the structure



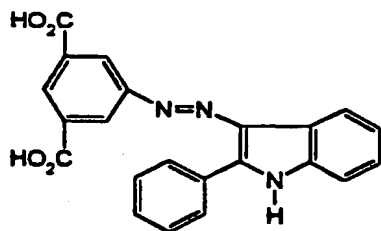
1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.5 g) and DMF (20 mL) was heated at about 95°C with occasional stirring for 5.0 hours. The reaction mixture was drowned into methanol. Acetic acid (1.0 mL) was added and the polydye was collected by filtration and washed with water and dried in air. GPC analysis indicated a Mw of 9,876, a Mn of 3,917 and a polydispersity of 2.52. An absorption maximum at 506 nm was observed in the visible light absorption spectrum in DMF.

Example 77

20

A mixture of the diacidic azo compound (0.60 g, 0.00155 mole) having the structure

- 81 -



1,2-ethanediol, dimethanesulfonate (0.34 g, 0.00155 mole), potassium carbonate (0.3 g) and DMF (4.0 mL) was heated at about 95°C for 4.0 hours. The reaction mixture was
5 drowned into methanol (20 mL) and the yellow polydye was collected by filtration, washed with methanol, water containing acetic acid, water and then air dried (yield - 0.5 g). GPC analysis showed a Mw of 4,566, a Mn of 2,474 and a Mw/Mn of 1.84. In the visible light absorption
10 spectrum in DMF an absorption maximum was observed at 420 nm.

Example 77a

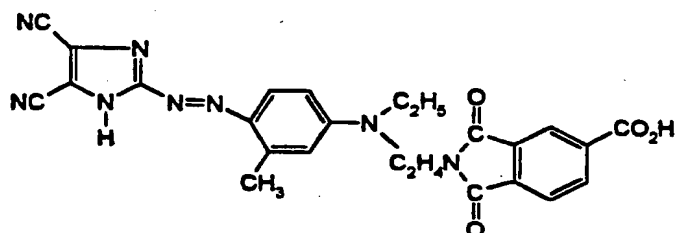
15 To a mixture of 3-(3',5'-dicarboxymethoxyphenylazo)-2-phenylindole (1.0 g, .00242 mole) in 2-ethoxyethanol (10 mL) was added aqueous 50% NaOH (0.75 g) and the hydrolysis reaction carried out by heating at about 95°C for 30 minutes. The reaction mixture was drowned into water (100
20 mL) and the solution treated with acetic acid to precipitate the product which was collected by filtration, washed with water and dried in air (yield - 0.85 g). FDMS indicated the structure to be that of the starting diacidic azo compound in Example 77.

25

Example 78

A mixture of the diacidic azo compound (0.99 g, 0.002 mole) having the structure

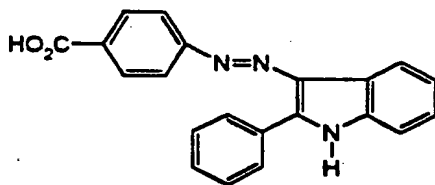
- 82 -



1,2-ethanediol, dimethanesulfonate (0.42 g, 0.002 mole),
 potassium carbonate (0.5 g) and DMF (7.0 mL) was heated at
 5 about 95°C for 3.0 hours. The reaction mixture was
 drowned into methanol (50 mL) and the scarlet polydye was
 collected by filtration, washed with methanol, water
 containing acetic acid, hot water and then dried in air
 (yield - 0.18 g). GPC analysis indicated a Mw of 8,246, a
 10 Mn of 2,619 and a polydispersity of 3.15.

Example 79

A mixture of the diacidic azo dye (2.50 g, 0.00733 mole)
 15 having the following structure



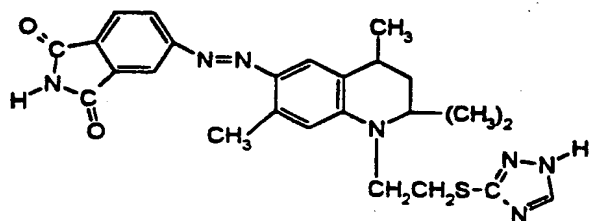
1,2-ethanediol, dimethanesulfonate (1.60 g, 0.00733 mole),
 potassium carbonate (2.07 g) and DMF (25 mL) was heated at
 20 95°C for 3.0 hours. The reaction mixture was drowned into
 methanol and a small amount of acetic acid added. The
 yellow polydye was collected by filtration, washed with a
 little methanol, water containing acetic acid, hot water
 and dried in air. GPC analysis indicated a Mw of 1,949, a

- 83 -

Mn of 1,569 and a Mw/Mn of 1.24. An absorption maximum was observed at 411 nm the visible light absorption spectrum.

5 Example 80

A mixture of the diacidic azo compound (1.22 g, 0.0025 mole) having the structure



10

1,2-ethanediol, dimethanesulfonate (0.55 g, 0.0025 mole), potassium carbonate (0.75 g) and DMF (8.0 mL) was heated and stirred at about 95°C for 3 hours with occasional stirring. The reaction mixture was drowned into methanol (50 mL) and the polydye was collected by filtration washed with methanol, water containing acetic acid, hot water and then dried in air (yield - 0.68 g). GPC analysis indicated a Mw of 2,259, a Mn of 1,571 and a Mw/Mn of 1.44. An absorption maximum was observed at 503 nm in DMF

15

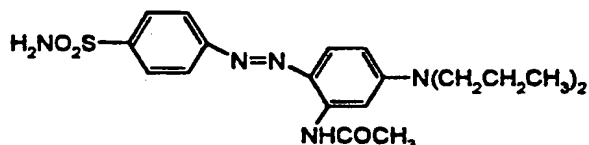
20 in the visible light absorption spectrum.

Example 81

A mixture of the diacidic azo compound (1.25 g, 0.003 mole) having the structure

25

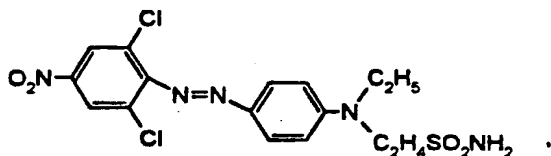
- 84 -



1,2-ethanediol, dimethanesulfonate (0.65 g, 0.003 mole), potassium carbonate (1.0 g) and DMF (10 mL) was heated at about 95°C for 3.0 hours with occasional stirring. The reaction mixture was drowned into methanol (25 mL) and the orange polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 0.75 g). GPC analysis indicated a Mw of 2,014, a Mn of 1,520 and a Mw/Mn of 1.32. An absorption maximum was observed at 493 nm in the visible light absorption spectrum in DMF.

Example 82

A mixture of the diacidic azo compound (1.11 g, 0.0025 mole) having the structure



1,2-ethanediol, dimethanesulfonate (0.55 g, 0.0025 mole), potassium carbonate (0.80 g and DMF (8.0 mL) was heated at about 95°C for 2.5 hours. The reaction mixture was drowned into methanol (100 mL) and the brown polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 0.30 g). GPC analysis indicated a Mw of 2,301, a Mn of 1,345 a Mw/Mn of 1.71. In the visible light absorption

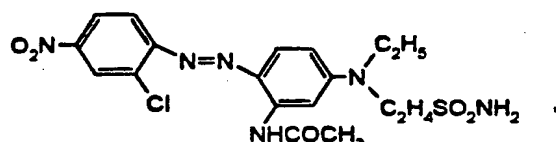
- 85 -

spectrum in DMF a maximum absorption was observed at 434 nm.

Example 83

5

A mixture of the diacidic azo compound (2.40 g, 0.005 mole) having the structure

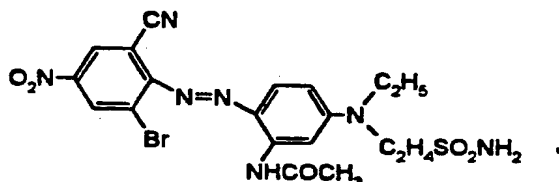


- 1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole),
10 potassium carbonate (1.5 g) and DMF (25 mL) was heated at
about 95°C for 3.0 hours with occasional stirring. The
reaction mixture was drowned into methanol (200 mL) and
the dark red polydye was collected by filtration, washed
with methanol, water containing acetic acid, hot water and
15 then dried in air (yield - 1.80 g). GPC analysis
indicated Mw of 2,914, a Mn of 809 and a Mw/Mn of 3.60.
An absorption maximum at 528 nm was observed in the
visible light absorption spectrum in DMF.

20 Example 84

A mixture of the diacidic azo compound (1.07 g, 0.002 mole) having the structure

- 86 -



1,2-ethanediol, dimethanesulfonate (0.44 g, 0.002 mole), potassium carbonate (0.5 g) and DMF (10 mL) was heated at 95°C with occasional stirring for 5 hours. The reaction mixture was drowned into methanol (50 mL) and the reddish-blue polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 0.83 g). GPC analysis indicated a Mw of 7,038, a Mn of 832 and a Mw/Mn at 8.44. An absorption maximum was observed at 574 nm in the visible light absorption spectrum in DMF.

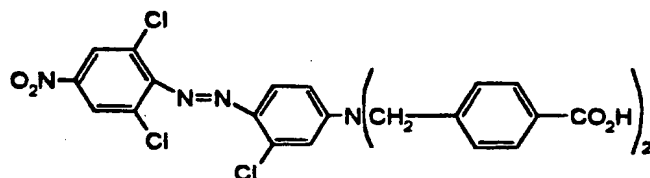
Example 85 - Displacement of Bromine in Polydye of Example 84 with Cyano Group

A mixture of a portion (0.5 g) of the polydye of Example 84, sodium dicyanocuprate (0.2 g) and DMF (8.0 mL) was heated at about 95°C with occasional stirring for 3.0 hours. The reaction mixture, the color of which changed from reddish-blue to neutral-blue as the displacement reaction occurred, was then drowned into methanol and the polydye was collected by filtration, washed with methanol and dried in air. GPC analysis indicated a Mw of 9,427, a Mw of 1,117 and a Mw/Mn of 8.44. An absorption maximum at 590 nm was observed in DMF in the visible light absorption spectrum.

Example 86

A mixture of diacidic azo compound (1.53 g, 0.0025 mole) having the structure

- 87 -



1,6-hexanediol, dimethanesulfonate (0.69 g, 0.0025 mole),
 K_2CO_3 (0.8 g) and DMF (8.0 mL) was heated at about 95°C
 5 with occasional stirring for 2.0 hours. The reaction
 mixture was drowned into methanol (100 mL) and the brown
 polydye was collected by filtration, washed with methanol,
 water containing acetic acid, hot water and then dried in
 air (yield - 0.62 g). GPC analysis indicated a Mw of
 10 4,795, a Mn of 2,051 and a Mw/Mn of 2.33. An absorption
 maximum at 434 nm in DMF was observed in the visible light
 absorption spectrum.

Example 86a

15 To conc. H_2SO_4 (33.0 mL) was added 2,6-dichloro-4-
 nitroaniline (6.21 g, 0.03 mole) with stirring. The
 solution was cooled to 0-5°C and stirred while a nitrosyl
 sulfuric acid mixture, prepared by adding sodium nitrite
 20 (2.19 g) to conc. H_2SO_4 (15 mL) portionwise with stirring
 and allowing the temperature to rise, was added below 5°C
 with stirring. The diazotization reaction mixture was
 stirred at 0-5°C for 2.0 hours. An aliquot of the
 diazonium salt solution (0.01 mole) was added to a chilled
 25 solution of the diacid coupler (3.95 g, 0.01 mole) (N,N-
 bis(4-carboxyphenylmethyl)-3-chloroaniline) dissolved in
 1:5 (1 part propionic acid:5 parts acetic acid) (120 mL)
 containing some conc. HCl (5.0 mL) with stirring at 0-5°C.
 The coupling reaction mixture was neutralized by the
 30 addition of ammonium acetate with stirring and allowed to
 stand with occasional stirring at below 5°C for about 1.0

- 88 -

hour. Water was added to precipitate the solid dye, which was collected by filtration, washed with water and dried in air (yield - 4.0 g). The crude dye was reslurried in hot methanol and the mixture allowed to cool. The final dye was collected by filtration, washed with methanol and dried in air. An absorption maximum was observed at 431 nm in DMF. The diacid dye was used as the starting material in Example 86.

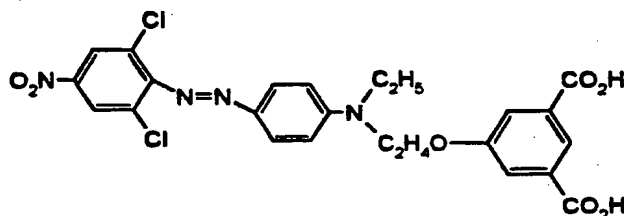
10 Example 86b

A mixture of m-chloroaniline (2.56 g, 0.02 mole), methyl 4-(bromomethyl)benzoate (10.08 g, 0.044 mole), sodium carbonate (4.66 g) and sodium iodide (0.2 g) and 2-ethoxyethanol (50 mL) was heated under nitrogen at about 90°C for 3.0 hours with stirring. The reaction mixture was drowned into water and the product was extracted into methylene chloride. Methylene chloride was removed to leave an oily product (11.0 g), which was added to 2-ethoxyethanol (100 mL). To the solution was added aqueous 50% NaOH solution (7.50 g) and the reaction mixture was warmed. At about 30°C, white solids began to precipitate and at about 50°C the reaction mixture become very thick. When the temperature had reached 70°C, water (20 mL) was added to dissolve the salts of the diacidic product. After stirring at 70°C for 1.5 hours the reaction mixture was clarified by filtering through Celite filter aid and the filtrate acidified by the addition of 10% aqueous HCl to pH of about 4.0. The white solid was collected by filtration, washed with water and dried in air (yield - 7.20 g). FDMS indicated the product to have the structure of the coupler used in Example 86a.

- 89 -

Example 87

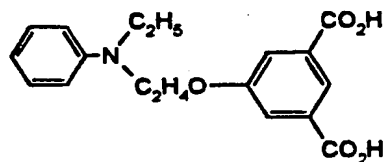
A mixture of the diacidic azo compound (1.64 g, 0.003 mole) having the structure



5 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at about 95°C for 25 hours with occasional stirring. The reaction mixture was drowned into methanol (150 mL) and
 10 the polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 1.5 g). GPC analysis indicated a Mw of 2,741, a Mn of 1,367 and a Mw/Mn of 2.00. An
 15 absorption maximum at 441 nm was observed in the visible light absorption spectrum in DMF.

Example 87a

20 An aliquot (0.01 mole) of the diazonium salt from 2,6-dichloro-4-nitroaniline prepared in Example 86a was added to a chilled solution of the coupler (3.29 g, 0.01 mole) having the formula



- 90 -

dissolved in 1:5 acid (100 mL) with stirring at 0-5°C. Ammonium acetate was added with stirring until the coupling mixture was neutral to Congo Red Test paper. After allowing to stand for 1.0 hour, water was added to
5 the coupling mixture to precipitate the dye, which was collected by filtration, washed with water and dried in air (yield - 4.27 g). An absorption maximum was observed at 460 nm in the visible light absorption spectrum in DMF.

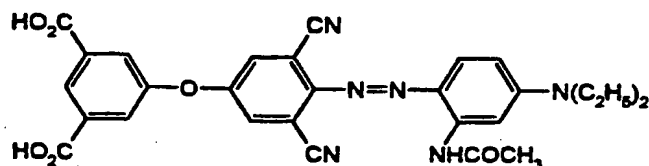
10 Example 87b

A mixture of N-(2-chloroethyl)-N-ethylaniline (46.0 g, 0.25 mole), dimethyl 5-hydroxyisophthalate (52.5 g, 0.25 mole), potassium carbonate (69.08), a trace of pulverized
15 potassium iodide and DMF (350 mL) was heated at 125-30°C for 3.5 hours with stirring. The reaction mixture was allowed to cool and drowned in water/ice mixture (1.0 L). The product separated as a brown oil and the aqueous layer was removed by decantation. To the oily product was added
20 2-ethoxyethanol (175 mL) and aqueous 50% NaOH (50.0 g) and the hydrolysis reaction mixture was heated at 60-65°C for about 20 minutes. Acetone was added to the reaction mixture and the white solid was collected by filtration, washed with acetone and dried in air (yield - 99.0 g).
25 The disodium salt was dissolved in water (250 mL) by stirring. Acidification with conc. HCl to a pH of about 3.0 gave a slightly sticky product which solidified in a few minutes. The pale yellow granular solid was collected by filtration, washed with water and dried in air (yield -
30 58.0 g). FDMS indicated the structure to be that of the coupler used in Example 87a.

Example 88

35 A mixture of the diacid azo compound (0.70 g, 0.0013 mole) having the structure

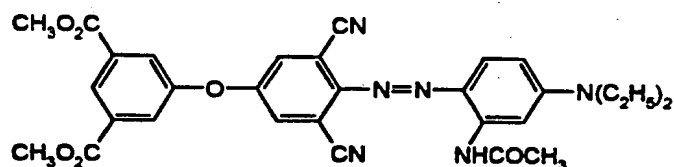
- 91 -



1,6-hexanediol, dimethanesulfonate (0.36 g, 0.0013 mole), potassium carbonate (0.35 g) and DMF (5.0 mL) was heated at about 95°C with occasional stirring for 2.0 hours. The reaction mixture was drowned into methanol (50 mL) and the polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 0.55 g). GPC indicated a Mw of 7,353, a Mn of 2,431 and a Mw/Mn of 3.02. An absorption maximum at 537 nm was observed in the visible light absorption spectrum in DMF.

Example 88a

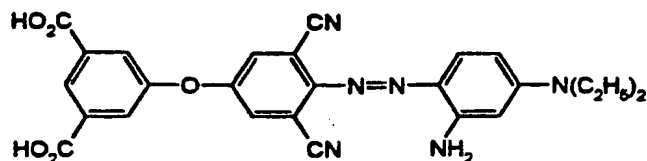
To a mixture of the diester dye (1.75 g, 0.0013 mole) having the structure



and 2-ethoxyethanol (20 mL) was added aqueous 50% NaOH solution (1.2 g) and the hydrolysis mixture was heated at about 10 minutes at about 95°C. The reaction mixture was drowned into acetone and the solid material collected by filtration. The acetone-wet material was dissolved by stirring in water (200 mL) and the diacid dye precipitated by adding acetic acid. The product was collected by

- 92 -

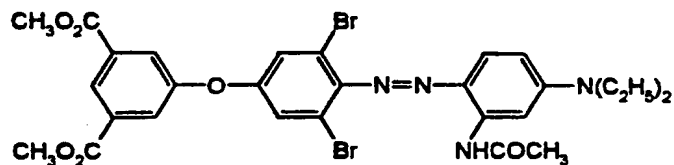
filtration washed with water and dried in air (yield - 1.35 g). FDMS showed the product to be mostly



- 5 indicating hydrolysis of the acetamido group in addition to the ester group. All of the product was added to acetic acid (8.0 mL) and acetic anhydride (1.0 mL). The reaction mixture was heated at 95°C for 30 minutes with occasional stirring. A bathochromic shift in color from
- 10 red to magenta was observed as the amine group was acetylated. The reaction mixture was allowed to cool, whereupon a solid dark red product crystallized, and then was drowned into methanol (40 mL). The product was collected by filtration, washed with water and dried in
- 15 air (yield - 0.90 g). FDMS indicated the structure to be that of the diacidic azo dye in Example 88.

Example 88b

- 20 A mixture of the dibromo azo dye (3.00 g, 0.0044 mole) having the structure



- 25 sodium dicyanocuprate (0.69 g, 0.005 mole) and DMF (30 mL) was heated at 95°C for 1.0 hour. The reaction mixture was drowned into methanol (150 mL) and the dye was collected

- 93 -

by filtration, washed with methanol and dried in air (yield - 1.91 g). FDMS indicated the structure to be that of the dicyano dye used in Example 88a.

5 Example 88c

To conc. H_2SO_4 (7.5 mL) was added dry NaNO_2 (1.08 g) portionwise with stirring and the temperature allowed to rise. The nitrosyl sulfuric acid mixture was cooled and
10 1:5 acid (15 mL) was added at less than 10°C with stirring. To this mixture was added at $0-5^\circ\text{C}$ with stirring dimethyl 5-(4'-amino,2',6'-dibromophenoxy)isophthalate (6.86 g, 0.015 mole), followed by an additional 15 mL of 1:5 acid. The diazotization
15 reaction mixture was stirred at $0-5^\circ\text{C}$ for 2.0 hours and then an aliquot (0.0075 mole) was added to a solution of 3-acetamido-N,N-diethylaniline (1.54 g, 0.0075 mole) dissolved in 1:5 acid (75 mL) at $0-5^\circ\text{C}$. Ammonium acetate was added with stirring to the coupling mixture until
20 neutral to Congo Red test paper. Coupling was allowed to continue at $0-5^\circ\text{C}$ for 1.0 hour and the dye then precipitated by addition of water, collected by filtration, washed with water and dried in air. FDMS indicated the structure to be that of the starting dibromo
25 azo dye in Example 88b. An absorption maximum at 546 nm was observed in the visible light absorption spectrum in DMF.

Example 88d

30

A mixture of the dimethyl 5-(4'-aminophenoxy)isophthalate (15.0 g, 0.05 mole) (Example 12c), anhydrous sodium acetate (9.6 g) and acetic acid (85 mL) was treated with stirring with bromine (17.4 g, 0.11 mole) allowing the
35 temperature to rise. The reaction mixture was heated at $70-80^\circ\text{C}$ for 1.5 hours, allowed to cool, and then drowned

- 94 -

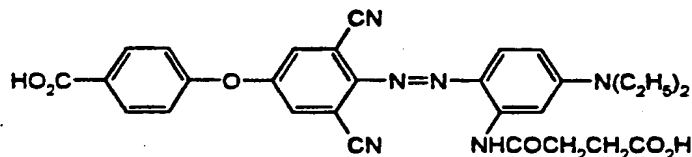
into ice water (350 mL). The product was collected by filtration, washed with water and dried in air (yield - 21.9 g). FDMS indicated the structure to be that of the amine compound diazotized in Example 88c.

5

Example 89

A mixture of the diacidic azo compound (1.39 g, 0.0025 mole) having the structure

10



1,6-hexanediol, dimethanesulfonate (0.68 g, 0.0025 mole), potassium carbonate (1.0 g) and DMF (8.0 mL) was heated at 95°C for 2.5 hrs with occasional stirring. The reaction mixture was drowned into methanol (100 mL) and the red polydye was collected by filtration, washed with water containing acetic acid, hot water and dried in air (0.85 g). GPC analysis indicated a Mw of 2,772, a Mn of 1,306 and a Mw/Mn of 2.12. An absorption maximum was observed at 538 nm in the visible light absorption spectrum in DMF.

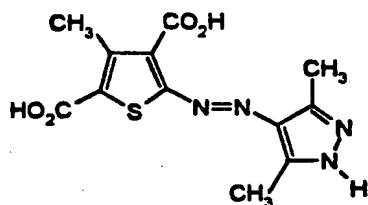
20

Example 90

A mixture of the diacidic azo compound (1.23 g, 0.004 mole) having the formula

25

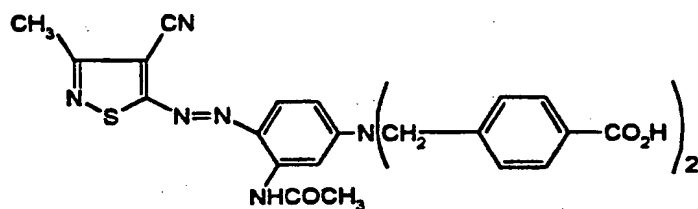
- 95 -



1,2-hexanediol, dimethanesulfonate (1.1 g, 0.004 mole),
 potassium carbonate (0.55 g) and DMF (8.0 mL) was heated
 at 95°C for 1 hour. The reaction mixture was drowned into
 5 water (250 mL) containing acetic acid (5.0 mL). The
 yellow polydye was collected by filtration, washed with
 water and dried in air (yield - 1.21 g). GPC analysis
 indicated a Mw of 1,726, a Mn of 1,079 and a Mw/Mn of 1.6.
 An absorption maximum at 400 nm was observed in the
 10 visible light absorption spectrum in DMF.

Example 91

A mixture of the diacidic azo compound (1.71 g, 0.003
 15 mole) having the formula



1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole),
 potassium carbonate (0.85 g) and DMF (8.0 mL) was heated
 20 with occasional stirring at 95°C for 2.0 hours. The
 reaction mixture was drowned into methanol (100 ml) and
 the red polydye was collected by filtration, washed with
 methanol, water containing acetic acid, hot water and

- 96 -

dried in air (yield- 1.5 g). GPC indicated a Mw of 2,090, a Mn of 1,235 and a Mw/Mn of 1.69. An absorption maximum was observed at 545 nm in the visible light absorption spectrum in DMF.

5

Example 91a

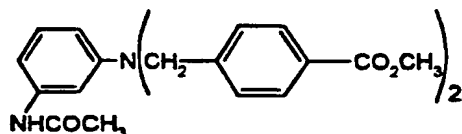
To conc. H_2SO_4 (5.0 mL) was added dry NaNO_2 (0.72 g) portionwise with stirring, allowing the temperature to
10 rise. The nitrosyl sulfuric acid solution was stirred and cooled and 1:5 acid (10 ml was added below about 15°C, followed by 5-amino-4-cyano-3-methylisothiazole (1.39 g, 0.01 mole) and 1:5 acid (10 ml) both added at 0-5°C. After being stirred at 0-5°C for 2.0 hours an aliquot
15 (0.005 mole) of the diazonium solution was added to a stirred solution of 3-acetamido-N,N-bis-(4-carboxyphenylmethyl)aniline (2.09 g, 0.005 mole) dissolved in 1:5 acid (30 ml) at 0-5°C. Ammonium acetate was added to neutralize the coupling mixture until neutral to Congo
20 Red test paper. Water was added to the coupling mixture to precipitate the red dye, which was collected by filtration and dried in air (yield- 2.67 g). The product was reslurried in hot methanol, allowed to cool and the solid collected by filtration, washed with methanol and
25 dried in air (yield- 2.10 g). FDMS indicated the structure to be that of the diacid azo compound used as a starting material for Example 91.

Example 91b

30

To a slurry of the diester compound (12.00 g, 0.0269 mole) having the structure

- 97 -

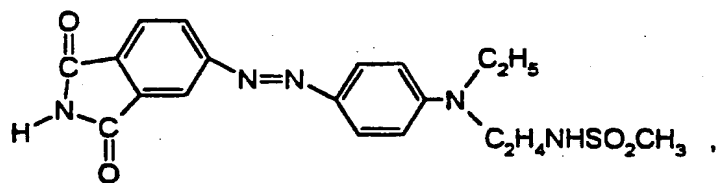


in water (150 ml) was added aqueous 50% NaOH solution (10.80 g) and 2-ethoxyethanol (20 ml). The reaction mixture was heated at about 70-80°C for 2.0 hours and
 5 allowed to cool. The cloudy reaction mixture was clarified by filtering through Celite filter aid and the filtrate was drowned into ice/water mixture (150 g). Conc. HCl was added dropwise with stirring to bring the pH to about 2.5. The tan solid was collected by filtration,
 10 washed with water and dried at 40°C under nitrogen (yield-10.04 g). FDMS indicated the product to have the structure of the coupler used in Example 91a.

Example 92

15

A mixture of the diacidic azo compound (0.83 g, 0.002 mole) having the structure



20 1,2-ethanediol, dimethanesulfonate (0.44 g, 0.002 mole), potassium carbonate (0.5 g) and DMF (7.5 ml) was heated at about 95°C for 3.0 hours. The polydye was isolated by drowning the reaction mixture into water and acidifying with acetic acid, followed by filtering, washing with
 25 water and drying in air. GPC analysis indicated a Mw of 2,379, a Mn of 1,363 a Mw/Mn of 1.74. An absorption

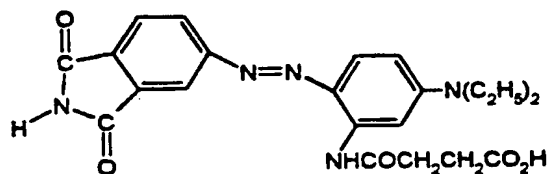
- 98 -

maximum was observed in DMF in the visible absorption spectrum at 480 nm.

Example 93

5

A mixture of the diacidic azo compound (1.26 g, 0.003 mole) having the structure

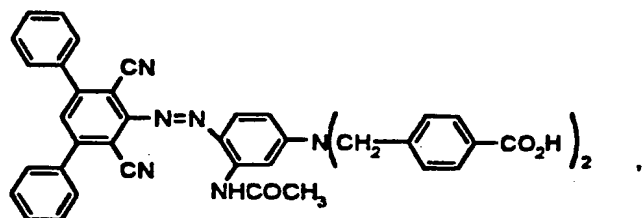


- 10 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.50 g) and DMF (8.0 mL) was heated at about 95°C for 1.5 hours. The reaction mixture was drowned into methanol (100 mL) and acetic acid (1.0 mL) was added. The initially sticky polydye solidified after
- 15 standing for about 1.0 hour and was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 0.60 g). GPC analysis indicated a Mw of 2,667, a Mn of 1,695 and a Mw/Mn of 1.57. An absorption maximum at 508 nm was
- 20 observed in the visible light absorption spectrum in DMF.

Examples 93a

- 25 A mixture of the diacidic azo compound (3.62 g, 0.005 m) having the structure

- 99 -



1,2-ethanediol, dimethanesulfonate (1.10 g, 0.005 m),
 potassium carbonate (1.50 g) and DMF (30 mL) was heated at
 5 about 95°C with stirring for 2.0 hours. The reaction
 mixture was drowned into methanol (100 mL) and the red
 polydye was collected by vacuum filtration and washed with
 methanol, water containing acetic acid, hot water and
 dried in air (yield- 3.08 grams). GPC analysis indicated
 10 a Mw of 7,176, a Mn of 3,533 and a Mw/Mn of 2.02. An
 absorption maximum was observed in the visible light
 absorption spectrum at 525 nm.

Example 93b

15 To conc. H₂SO₄ (5.0 mL) was added dry NaNO₂ (0.72 g)
 portionwise with stirring, allowing the temperature to
 rise. The nitrosyl sulfuric acid solution was stirred and
 cooled and 1:5 acid (1 part propionic:5 parts acetic acid)
 20 (10 mL) was added below about 15°C, followed by 2,6-
 dicyano-3,5-diphenylaniline (2.95 g, 0.01 m) and 1:5 acid
 (10 mL) both added at 0-5°C. After being stirred for 2.0
 hours at 0-5°C, the diazonium solution was added to a
 stirred solution of 3-acetamido-N,N-bis (4-
 25 carboxyphenylmethyl)aniline (4.18 g, 0.01 m) dissolved in
 a mixture of 1:5 acid (75 mL) plus 15% aqueous sulfuric
 acid (15 mL) at 0-5°C. Ammonium acetate was added
 portionwise until the coupling mixture was neutral to
 Congo Red test paper. After about 1.0 hour, water was
 30 added to the coupling mixture and the resulting slurry

- 100 -

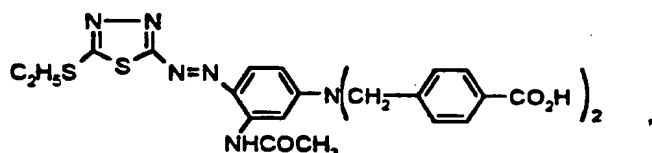
heated to about 60°C. The red product was collected by filtration, washed well with hot water and dried in air (yield - 5.43 g). FDMS analysis indicated the structure to be that of the starting material for Example 93-1.

5

Example 93c

A mixture of the diacidic azo compound (1.80 g, 0.003 m) having the structure

10



1,2-ethanediol, dimethanesulfonate (0.66 g, 0.003 m), potassium carbonate (1.0 g) and DMF (8 mL) was heated at about 95°C with occasional stirring. The polydye was isolated by drowning the reaction mixture into methanol (100 mL) followed by filtration and washing with methanol, water containing acetic acid, water and was then dried in air (yield - 0.52 g). GPC analysis using NMP (N-methyl-2-pyrrolidinone) solvent indicated a Mw of 5,413, a Mn of 2,196 and a Mw/Mn of 2.46. An absorbance maximum at 517 nm was observed in the visible absorption maximum in DMF.

25 Example 93d

A sample of 2-amino-5-ethylthio-1,3,4-thiadiazole (1.61 g, 0.01 m) was diazotized and coupled with 3-acetamido-N,N-bis(4-carboxyphenylmethyl)aniline (4.18 g, 0.01 m) and the red product isolated using the procedure described above in Example 93-1a. FDMS indicated the structure of the azo compound to be that of the starting material for Example 93-2.

30

- 101 -

Examples 94-118

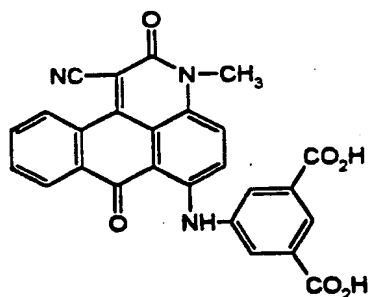
Colored EASTAR® PETG 6763 film was produced by melt
5 blending the polydyes of Examples 69-93 and extruding
according to the following procedures to produce Examples
94-118 (Table 2).

EASTAR® PETG polyester 6763, a
10 poly(ethylene-cyclohexanedimethylene) terephthalate
(Eastman Chemical Company) (300 g of previously dried
pellets) was dry blended with the azo dye composition
(0.12 g) and the blend extruded and finally a 18-20 mil
thick film prepare as described above for Examples 37-66.

15

Example 119

A mixture of the diacidic anthrapyridone compound (0.93 g,
0.002 mole) having the structure



20

1,2-ethandiol, dimethanesulfonate (0.44 g, 0.002 mole),
potassium carbonate (.5 g) and DMF (8.0 mL) was heated at
about 95°C for 3.0 hours with occasional stirring. The
25 reaction mixture was drowned into methanol (100 mL) and
the violet polydye was collected by filtration, washed

- 102 -

with methanol, water containing acetic acid, water and dried in air (yield - 1.09 g). A number average molecular weight of 1,228 was obtained by GPC analysis. Absorption maxima at 544 and 583 nm were observed in the visible light absorption spectrum in DMF.

Example 119a

To a mixture of 1-cyano-6-(3',5'-dicarbomethoxyphenylamino)-3-methyl-3H-dibenz[f,i]isoquinoline-2,7-dione (2.00 g, 0.00405 mole) stirred in 2-ethoxyethanol (50 mL) was added aqueous 50% NaOH solution (2.47 g). The reaction mixture was heated at 90-95°C for 50 minutes and then was drowned into water. The mixture was acidified by addition of acetic acid and the solid product was collected by filtration, washed with water and dried in air (yield - 1.78 g). FDMS indicated the product to be the diacidic anthrapyridone compound reacted in Example 119.

20

Example 119b

A mixture of 6-bromo-1-cyano-3-methyl-3H-dibenz[f,i]isoquinoline-2,7-dione (11.0 g, 0.03 mole), dimethyl 5-aminoisophthalate (25.1 g, 0.12 mole), cupric acetate (3.6 g), potassium carbonate (3.0 g) and DMF (90 mL) was heated and stirred under nitrogen to about 135-40°C. The reaction mixture became very thick and turned violet. Additional DMF (40 mL) was added and heating was continued at 135-40°C for 2.0 hours. The reaction mixture was allowed to cool to about 60°C and poured on a coarse fritted glass funnel for vacuum filtration. The product was washed with DMF and water and the water-wet cake was reslurried in boiling acetone (250 mL). After cooling, the product was collected by filtration, washed with acetone and dried in air (yield - 10.8 g). FDMS indicated

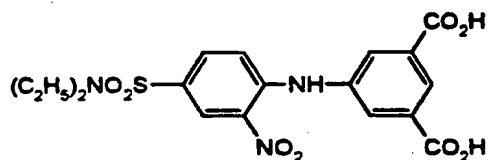
- 103 -

the product to be the diester anthrapyridone compound used in Example 119a.

Example 120

5

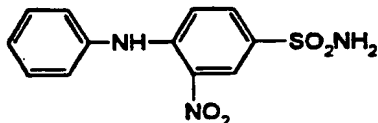
A mixture of the diacidic nitroarylamine compound (2.50 g, 0.0057 mole) having the structure



1,2-ethanediol, dimethanesulfonate (1.25 g, 0.0057 mole),
10 potassium carbonate (1.6 g) and DMF (15 mL) was heated at
95°C for 2.5 hours. The reaction mixture was drowned into
methanol (200 mL) and the yellow polydye was collected by
filtration, washed containing acetic acid, water and dried
at 40°C (yield - 0.77 g). An absorption maximum was
15 observed at 412 nm in the visible absorption spectrum in
DMF.

Example 121

20 A mixture of the diacidic nitroarylamine compound (4.40 g,
0.015 mole) having the structure



1,2-ethanediol, dimethanesulfonate (3.27 g, 0.015 mole),
25 potassium carbonate (2.0 g) and DMF 40 mL) was heated at
90-95°C with stirring for 4.0 hours. The reaction
mixture was drowned into methanol (200 mL) and the yellow
polydye was collected by filtration, washed with methanol,

- 104 -

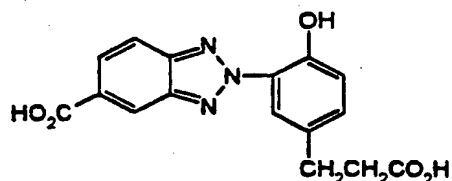
water containing acetic acid, water and dried in air
(yield - 1.80 g). GPC analysis indicated a Mw of 1,585, a
Mn of 1,024, a Mw/Mn of 1.54. An absorption maximum at
416 nm was observed in the visible light absorption
5 spectrum in DMF.

Examples 122-124

Colored polyester film was produced by melt blending and
10 extruding EASTAR® PETG polyester 6763 (Eastman Chemical
Company) (300 g previously dried pellets) which had dry
blended with the polydyes of Examples 119, 120, 121 to
produce Examples 122-124, respectively, according to the
procedure used to produce Examples 37-66. The film of
15 Example 122 was violet and those of Examples 123 and 124
were bright yellow.

Example 125

20 A mixture of the benzotriazole UV light absorbing compound
(3.27 g, 0.01 mole) having the structure



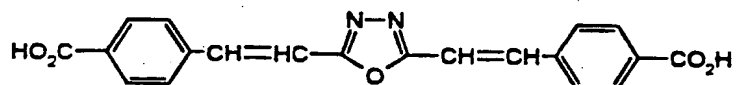
1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole),
potassium carbonate (2.76 g) and DMF (25 mL) was heated at
25 about 95°C for 6.0 hours. The reaction mixture was
drowned into methanol (200 mL) and a little acetic acid
added. The polymeric UV light absorbing compound was
collected by filtration, washed with water containing a
little acetic acid, hot water and then dried in air (yield
30 - 2.88 g). GPC analysis indicated a Mw of 7,561, a Mn of

- 105 -

2,632 and a Mw/Mn of 2.87. An absorption maximum was observed at 350 nm in the UV light absorption spectrum in methylene chloride.

5 Example 126

A benzylidene type UV light fluorescent compound (1.0 g, 0.0028 mole) having the structure



- 10 1,6-hexenediol, dimethanesulfonate (0.0028 mole), potassium carbonate (0.97 g) and DMF (10 mL) were mixed and the reaction mixture was heated at for 3.0 hours at about 120-130°C. The reaction mixture was drowned into methanol (100 mL) and the polymer was collected by
- 15 filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 0.69 g). GPC indicated a Mw of 50,717, a Mn of 16,044 and a MW/Mn of 3.16.

20 Example 127

- EASTAPAK® PET 7352, a poly(ethyleneterephthalate) (Eastman Chemical Company) (400 g of previously dried pellets) was dry blended with the polymeric UV light fluorescent
- 25 material of Example 126 (0.16 g). The blend was extruded with a C. W. Brabender ¼ inch extruder, equipped with a mixing screw, at 285°C into a water bath and the extrudate pelletized. The pellets which contained about 400 ppm of the UV light absorber showed a strong blue white
- 30 fluorescence under UV light.

Example 128

- 106 -

Example 127 was repeated except that 8 mg of the UV light fluorescent material of Example 126 was added to the EASTAPAK® PET 7352. The resulting pellets showed a strong
5 blue-white fluorescence under UV light and appeared very white in sunlight.

Example 129

10 A mixture of Pc-Al-O-C₆H₃-3,5-diCO₂H (Pc = phthalocyanine) (1.74 g, 0.0024 mole), 1,6-hexanediol, dimethanesulfonate (0.66 g, 0.0024 mole), potassium carbonate (0.83 g) and DMF (10 mL) was heated and stirred at about 125°C for 1
15 hour and then at about 140°C for 1 hour. The reaction mixture was drowned into methanol (50 mL) and the polymeric product was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield - 1.48 g).

20 Example 130

EASTAPAK® PET 7352, a poly(ethyleneterephthalate) (Eastman Chemical Company) (400 g of previously dried pellets) was dry blended with the polymeric phthalocyanine compound of
25 Example 129 (0.12g). The blend was extruded with a C. W. Brabender ¼ inch extruder, equipped with a mixing screw, at 285° into a water bath and the extrudate pelletized. The cyan pellets were redried at 70°C for about 17 hrs at a pressure of about 1-5 torr. A portion of the dried
30 pellets (1.40 g) was pressed into a film at 285°C using a 2-inch diameter circular mold in a Pasadena Hydraulic, Inc. press using 12,000 pounds ram force (4-inch ram). A transparent cyan film was produced by quenching in water and had an absorption maximum at 684 nm in the light
35 absorption spectrum.

- 107 -

Example 131

Example 130 was repeated except that 4 mg of the polymeric phthalocyanine compound of Example 129 was added to the
5 PET . The final film contained about 10 ppm and had a light absorption maximum at 685 nm.

Example 132

10 EASTAPAK® PET 7352, a poly(ethyleneterephthalate) (Eastman Chemical Company) (400 g of dried pellets) was dry blended with the polydye of Example 18 (0.6 g). The blend was extruded with a C. W. Brabender $\frac{3}{4}$ inch extruder, equipped with a mixing screw, at 285°C into a water bath and the
15 extrudate pelletized. Good color production resulted with no evidence of color loss by sublimation to give dark red pellets containing about 0.15% by weight of the polydye.

Example 133

20 Example 132 was repeated using 0.6 g of the polydye of Example 75 as the colorant to give yellow pellets having about 0.15% by weight of the polydye. No loss of color by sublimation was observed.

25

Examples 134-182

The diacidic azo compounds of Formula VI in Table 3 are reacted with essentially equimolar amounts of 1,2-
30 ethanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 134-182 in Table 3.

Examples 183-193

35

- 108 -

The diacidic diazo compounds of Formula VII in Table 4 are reacted with essentially equimolar amounts of 1,4-butanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 183-193 in Table 4.

Examples 194-202

The diacidic bisazo compounds of Formula VIIa in Table 5 are reacted with essentially equimolar amounts of 1,3-propanediol, dimethanesulfonate in DMF in the presence of sodium carbonate to yield the polydyes of Examples 194-202 in Table 5.

Examples 203-211

The diacidic benzylidene (methine) compounds in Table 6 are reacted with essentially equimolar amounts of 1,4-cyclohexanedimethanol, dimethanesulfonate in DMF in the presence of sodium carbonate to yield the polydyes of Examples 203-211 in Table 6.

Examples 212-220

The diacidic 3-aryl-2,5-dioxypyrroline compounds of Formula X in Table 7 are reacted with essentially equimolar amounts of diethylene glycol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 212-220 in Table 7.

30

Examples 221-230

The diacidic 3-aryl-5-dicyanomethylene-2-oxypyrroline compounds of Formula XI in Table 8 are reacted with essentially equimolar amounts of triethylene glycol,

- 109 -

dimethanesulfonate to yield the polydyes of Examples 221-230 in Table 8.

Examples 231-239

5 The diacidic azo-methine compounds of Formula XIII in Table 9 are reacted with essentially equimolar amounts of 1,4-butanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 10 231-239 in Table 9.

Examples 240-269

15 The diacidic anthraquinone compounds of Formula XIV in Table 10 are reacted with essentially equimolar amounts of 2,2,4,4-tetramethyl-1,3-cyclobutanediol, dimethanesulfonate in N,N-dimethylacetamide in the presence of potassium carbonate to yield the polydyes of 20 Examples 240-269 in Table 10.

Examples 270-326

25 The diacidic anthraquinone compounds of Formula XV in Table 11 are reacted with essentially equimolar amounts of 1,2-ethanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 270-326 in Table 11.

Examples 327-344

30 The diacidic anthraquinone compounds of Formula XVI in Table 12 are reacted with essentially equimolar amounts of 1,6-hexanediol, dimethanesulfonate in N-methyl-2-pyrrolidinone in the presence of sodium carbonate to yield 35 the polydyes of Examples 327-344 in Table 12.

- 110 -

Examples 345-361

5 The diacidic anthrapyridine compounds of Formula XVIII in Table 13 are reacted with essentially equimolar amounts of 1,4-butanediol, di-p-toluenesulfonate in the presence of DMF to yield the polydyes of Examples 345-361 in Table 13.

Examples 362-381

10 The diacidic anthraquinone compounds of Formula XIX in Table 14 are reacted with 2,2-dimethyl-1,3-propanediol, dimethanesulfonate in essentially equimolar amounts in DMF in the presence of potassium carbonate to yield the polydyes of Examples 362-381 in Table 14.

15

Examples 382-396

20 The diacidic anthraquinone compounds of Formula XIXc of Table 15 are reacted with essentially equimolar amounts of 1,2-ethanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 382-396 in Table 15.

Examples 397-414

25

The diacidic anthraquinone compounds of Formula XIXd in Table 16 are reacted with essentially equimolar amounts of 1,6-hexanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 30 397-414 in Table 16.

Examples 415-435

35 The diacidic anthraquinone compounds of Formula XIXe in Table 17 are reacted in essentially equimolar amounts with ethylene glycol, dimethanesulfonate in DMF in the presence

- 111 -

of potassium carbonate to yield the polydyes of Examples 414-435 in Table 17.

Examples 436-449

- 5 The diacidic anthraquinone compounds of Formula XIXf in Table 18 are reacted in essentially equimolar amounts with 1,4-cyclohexanedimethanol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 436-449 in Table 18.
- 10

Examples 450-455

- 15 The diacidic anthrapyridine compounds of Table 19 are reacted with essentially equimolar amounts of 1,6-hexanediol, di-p-toluenesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 450-455 in Table 19.

20 Examples 456-465

- The diacidic nitroarylamine compounds of Table 20 are reacted with 1,4-butanediol, dimethanesulfonate in essentially equimolar amounts in DMF in the presence of potassium carbonate to yield the polydyes of Examples 456-465 in Table 20.
- 25

Examples 466-505

- 30 The miscellaneous diacidic compounds of Table 21 are reacted with essentially equimolar amounts of the disulfonate compounds of Table 21 in DMF in the presence of potassium carbonate to yield the polydyes of Examples 466-505 in Table 21.

35

Examples 506-522

- 112 -

The diacidic UV light absorbing compounds of Table 22 are reacted with essentially equimolar amounts of the disulfonate compounds of Table 22 in DMF in the presence of potassium carbonate to yield the polymeric UV absorbers of Examples 506-522 in Table 22.

Examples 523-536

10 The diacidic infrared light absorbing compounds of Table 23 are reacted with essentially equimolar amounts of the disulfonate compounds of Table 23 in DMF in the presence of potassium carbonate to yield the polymeric infrared light absorbing compounds of Examples 523-536 in Table 23.

15

- 113 -

Table 1
Anthraquinone Polydyes in EASTAR® PETG
(300 ppm)

Example No.	Polydye Melt Blended and Extruded With EASTAR® PETG	Color of Film
37	Polydye of Example 7	Blue
38	Polydye of Example 8	Blue
39	Polydye of Example 9	Blue
40	Polydye of Example 10	Blue
41	Polydye of Example 11	Blue
42	Polydye of Example 12	Blue
43	Polydye of Example 13	Greenish-blue
44	Polydye of Example 14	Reddish-blue
45	Polydye of Example 15	Blue
46	Polydye of Example 16	Green
47	Polydye of Example 17	Bright blue
48	Polydye of Example 18	Bluish-red
49	Polydye of Example 19	Yellow
50	Polydye of Example 20	Orange
51	Polydye of Example 21	Red
52	Polydye of Example 22	Green
53	Polydye of Example 23	Yellow
54	Polydye of Example 24	Yellow
55	Polydye of Example 25	Yellow
56	Polydye of Example 26	Yellow
57	Polydye of Example 27	Blue
58	Polydye of Example 28	Red
59	Polydye of Example 29	Greenish-yellow
60	Polydye of Example 30	Yellow
61	Polydye of Example 31	Greenish-yellow
62	Polydye of Example 32	Blue
63	Polydye of Example 33	Yellow
64	Polydye of Example 34	Yellow
65	Polydye of Example 35	Greenish-blue
66	Polydye of Example 36	Greenish-blue

- 114 -

Table 2
Azo Polydyes in EASTAR® PETG 6763
(300 ppm)

Example No.	Polydye Melt Blended and Extruded With EASTAR® PETG	Color of Film
94	Polydye of Example 69	Violet
95	Polydye of Example 70	Blue
96	Polydye of Example 71	Yellow-brown
97	Polydye of Example 72	Red
98	Polydye of Example 73	Orange
99	Polydye of Example 74	Yellow
100	Polydye of Example 75	Greenish-yellow
101	Polydye of Example 76	Scarlet
102	Polydye of Example 77	Yellow
103	Polydye of Example 78	Scarlet
104	Polydye of Example 79	Yellow
105	Polydye of Example 80	Red
106	Polydye of Example 81	Orange
107	Polydye of Example 82	Reddish-brown
108	Polydye of Example 83	Red
109	Polydye of Example 84	Reddish-blue
110	Polydye of Example 85	Blue
111	Polydye of Example 86	Brown
112	Polydye of Example 87	Reddish-brown
113	Polydye of Example 88	Magenta
114	Polydye of Example 89	Magenta
115	Polydye of Example 90	Yellow
116	Polydye of Example 91	Red
117	Polydye of Example 92	Orange
118	Polydye of Example 93	Scarlet

- 115 -

Table 3
Polydyes From Diacidic Compounds of Formula VI

 $R_2 - N = N - Z$

Example No.	R_2	Z	Color
134			violet
135			red
136			magenta
137			violet
138			scarlet
139			red
140			violet

- 116 -

Table 3
Polydyes From Diacidic Compounds of Formula VI

 $R_4 - N = N - Z$

Example No.	R_4	Z	Color
141			blue
142			orange
143			scarlet
144			magenta
145			magenta
146			bluish-red
147			violet

- 117 -

Table 3
Polydyes From Diacid Compounds of Formula VI

 $R_3 - N = N - Z$

Example No.	R_3	Z	Color
148			blue
149			red
150			violet
151			violet
152			orange
153			red
154			navy blue

- 118 -

Table 3
Polydyes From Diacidic Compounds of Formula VI

 $R_2 - N = N - Z$

Example No.	R_2	Z	Color
155			blue
156			red
157			orange
158			red
159			blue
160			blue
161			red

- 119 -

Table 3
Polydyes From Diacidic Compounds of Formula VI

$$R_3 - N = N - Z$$

Example No.	R_3	Z	Color
162			red
163			red
164			orange
165			yellow
166			yellow
167			orange
168			yellow

- 120 -

Table 3
Polydyes From Diacidic Compounds of Formula VI






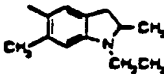
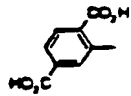
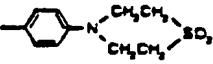
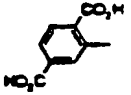
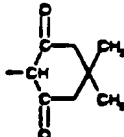
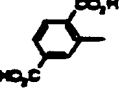
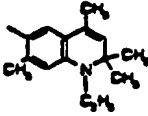
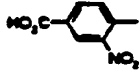
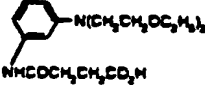
 $R_3 - N = N - Z$

Example No.	R_3	Z	Color
169			red
170			red
171			orange
172			blue
173			red
174			yellow
175			yellow

- 121 -

Table 3
Polydyes From Diacidic Compounds of Formula VI

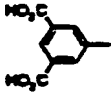

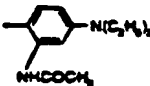

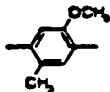
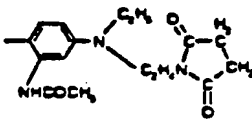
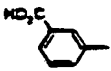




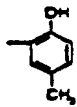


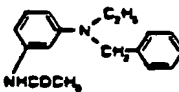
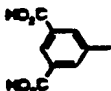

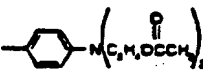
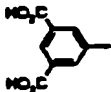
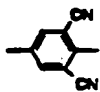
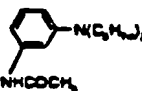


Example No.	R_2	Z	Color
176			yellow
177			yellow
178			orange
179			yellow
180			yellow
181			orange
182			red

- 122 -

Table 4
Polydyes From Diacidic Compounds of Formula VII



Example No.	R ₆	R ₇	Z	Color
183				red
184				red
185				reddish yellow
186				reddish yellow
187				red
188				yellow brown
189				blue

- 124 -

Table 5
Polydyes From Diacidic Compounds of Formula VIIa


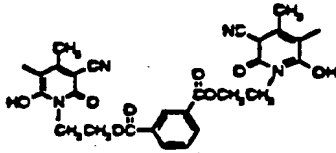
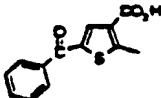
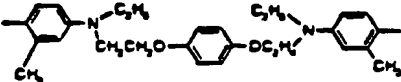


Example No.	R_2	Y_1	Color
194			red
195			orange
196			orange
197			orange
198			violet
199			red
200			violet

- 125 -

Table 5
Polydyes From Diacidic Compounds of Formula VIIa



Example No.	R_2	Y_1	Color
201			yellow
202			blue

- 126 -

Table 6
Polydyes From Diacid Compounds of Formula VIII


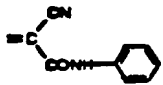
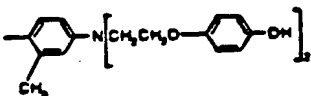
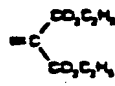
 $R_{11} - CH = D$

Example No.	R_{11}	D	Color
203			yellow
204			yellow
205			yellow
206			blue
207			yellow
208			red
209			red

- 127 -

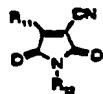
Table 6
Polydyes From Diacidic Compounds of Formula VIII

 $R_{11} - CH = D$

Example No.	R_{11}	D	Color
210			yellow
211			yellow

- 128 -

Table 7
Polydyes From Diacidic Compounds of Formula X



Example No.	R ₁₁	R ₁₂	Color
212		C ₂ H ₅	red
213		H	red
214		H	red
215		CH ₂ C ₆ H ₅	red
216		CH ₃	violet
217		CH ₂ CH ₂ OH	violet

- 129 -

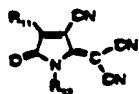
Table 7
Polydyes From Diacidic Compounds of Formula X



Example No.	R ₁₁	R ₁₂	Color
218			red
219			red
220		H	red

- 130 -

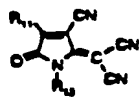
Table 8
Polydyes From Diacidic Compounds of Formula XI



Example No.	R_{11}	R_{12}	Color
221		H	blue
222		H	greenish blue
223		$CH_2CH=CH_2$	reddish blue
224		$CH_2C_6H_{11}$	blue
225		H	blue
226		H	blue

- 131 -

Table B
Polydyes From Diacidic Compounds of Formula XI



Example No.	R ₁₁	R ₁₂	Color
227		H	blue
228		H	blue
229		H	blue
230			blue

- 132 -

Table 9
 Polydyes From Diacidic Compounds of Formula XIII

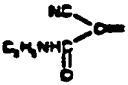

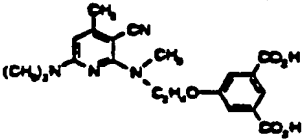
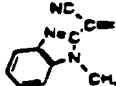
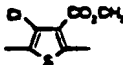
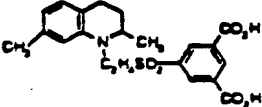
 $D = HC - R_7 - N = N - Z$

Example No.	D	R ₇	Z	Color
231				red
232				blue
233				blue
234				blue
235				blue
236				blue
237				blue

- 133 -

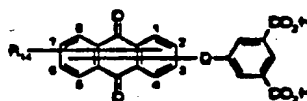
Table 9
Polydyes From Diacidic Compounds of Formula XIII

 $D = HC - R_7 - N = N - Z$

Example No.	D	R ₇	Z	Color
238				blue
239				blue

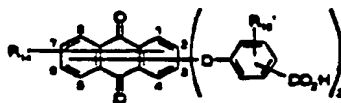
- 134 -

Table 10
Polydyes From Diacidic Anthraquinone Compounds of Formula XIV



Example No.	Q	R ₁₄	Color
240	5-S	1,4-diNHCH ₂ C(CH ₃) ₂ CH ₂ OH	blue
241	2-O-	1-NH ₂ , 4-OH	red
242	2-S-	1-NH ₂ , 4-NHSO ₂ CH ₃	violet
243	2-S-	1-NH ₂ , 4-NHSO ₂ C ₆ H ₅	violet
244	2-SO ₂ -	1-NH ₂ , 4-NHC ₆ H ₅	blue
245	2-SO ₂ -	1-NH ₂ , 4-NHC ₆ H ₄ -4-CH ₃	blue
246	2-SO ₂ -	1-NH ₂ , 4-SC ₆ H ₅	violet
247	2-S-	1-NH ₂ , 4-NHCOC ₆ H ₅	violet
248	4-S-	1-NH ₂	red
249	4-S-	1-NHC ₆ H ₁₁	violet
250	4-S-	1-NHC ₆ H ₅	violet
251	4-NH-	1-NH ₂ , 2-OC ₆ H ₅	violet
252	4-NH-	1-NHC ₆ H ₅	green
253	4-NH-	1-NHC ₆ H ₅ -2,6-diC ₂ H ₅	blue
254	4-NH-	1-OH	violet
255	2-S-	1,4-di-OH	orange
256	2-SO ₂ -	1,4-di-OH	orange
257	4-S-	1-NHCH ₃	violet
258	4-S-	1-NHCH ₂ CH(C ₂ H ₅)C ₆ H ₅	violet
259	6(7)S-	1,4-diNHC ₆ H ₅ -2,6-diC ₂ H ₅	cyan
260	6(7)S-	1,4-diNHC ₆ H ₅ -2,4,6-triCH ₃	cyan
261	6(7)SO ₂ -	1,4-diNHC ₆ H ₅ -2-CH ₃ ,6-C ₂ H ₅	cyan
262	4-NH-	1,8-diOH, 5-NO ₂	blue
263	4-NH-	1,8-diOH, 5-NH ₂	blue
264	4-NH-	1,8-diOH, 5-NHC ₆ H ₅	blue
265	4-NH-	1,5-diOH, 8-NO ₂	blue
266	4-NH-	1-NH ₂ , 2-CN	cyan
267	4-NH-	1-NH ₂ , 2-S-C ₆ H ₅	blue
268	4-NH-	1-NH ₂ , 2-S-C ₆ H ₄ -N ₂	blue
269	4-NH-	1-NH ₂ , 2-SO ₂ -C ₆ H ₃ Cl ₂	blue

Table 11
Polydyes From Diacidic Anthraquinone Compounds of Formula XV






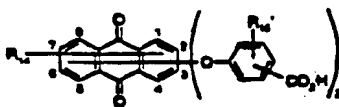
Example No.	$\left(\text{O} - \text{C}_6\text{H}_3(\text{CO}_2\text{H})_2 \right)_n$	R_{44}	Color
270	2,4-di-S-C ₆ H ₄ -3-CO ₂ H	1-NH ₂	red
271	2,3-di-S-C ₆ H ₄ -4-CO ₂ H	1,4-diNH ₂	blue
272	2,4-di-S-C ₆ H ₄ -2-CO ₂ H	1-NHCH ₃	violet
273	2-SO ₂ C ₆ H ₄ -2-CO ₂ H, 4-NHC ₆ H ₄ -2-CO ₂ H	1-NH ₂	blue
274	2-OC ₆ H ₄ -4-CO ₂ H, 4-NHC ₆ H ₄ -2-CO ₂ H	1-NH ₂	violet
275	2-OC ₆ H ₄ -3-CO ₂ H, 4-S-NHC ₆ H ₄ -2-CO ₂ H	1-NH ₂	red
276	2,4-di-S-C ₆ H ₄ -2-CO ₂ H	1-OH	orange
277	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHCH ₃	blue
278	4,5-di-S-C ₆ H ₄ -3-CO ₂ H	1,8-diNHCH ₂ CH(CH ₃) ₂	blue
279	4,5-di-S-C ₆ H ₄ -4-CO ₂ H	1,8-diNH(CH ₂) ₇ CH ₃	blue
280	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHCH ₂ (C ₂ H ₅)C ₂ H _{5-n}	blue
281	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHC ₆ H ₄ -4-CH ₃	blue
282	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHC ₆ H ₁₁	blue
283	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNH(CH ₂) ₃ OH	blue
284	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHCH ₂ C(CH ₃) ₂ CH ₂ OH	blue
285	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHCH ₂ C ₆ H ₅	blue
286	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHCH ₂ CH ₂ C ₆ H ₅	blue
287	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHCH ₂ CH=CH ₂	blue
288	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHCH ₂ C≡CH	blue
289	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHCH ₂ -  -CH ₂ OH	blue
290	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNHC ₂ H ₅	blue
291	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNHCH ₂ CH(CH ₃)CN	blue
292	4,8-di-S-C ₆ H ₄ -4-CO ₂ H	1,5-diNHCH ₂ CH ₂ NHCOCH ₃	blue
293	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNH(CH ₂) ₃ OC ₂ H ₅	blue
294	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNHCH ₂ C ₆ H ₁₀ -4-CH ₃	blue
295	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNHCH ₂ - 	blue
296	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNHCH ₂ - 	blue
297	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNH(CH ₂) ₃ OC ₆ H ₅	blue
298	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNHCH(CH ₃)(CH ₂) ₂ C ₆ H ₅	blue
299	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNHCH(CH ₂ CH ₃) ₂	blue

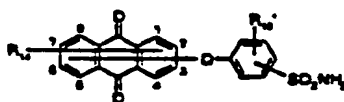
Table 11
Polydyes From Diacidic Anthraquinone Compounds of Formula XV



Example No.	$\left(\text{O} - \text{C}_6\text{H}_4 - \text{CO}_2\text{H} \right)_n$	R_{14}	Color
300	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diSCH ₂ CH ₂ OH	red
301	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diSCH ₂ C ₆ H ₅	red
302	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diSC ₆ H ₅	red
303	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diSC ₆ H ₁₁	red
304	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diSC ₆ H ₄ -4-OCH ₃	red
305	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diSC ₆ H ₄ -4-Cl	red
306	4,5-di-S-C ₆ H ₄ -3-CO ₂ H	1,8-diSC ₆ H ₄ -4-CH ₃	red
307	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diSC ₆ H ₄ -3,4-diCl	red
308	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diSC ₆ H ₄ -2-NHCOCH ₃	red
309	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diSC ₆ H ₄ -4-NHCOC ₆ H ₅	red
310	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diSCH ₂ CH ₂ OCOCH ₃	red
311	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diSC ₆ H ₄ -4-C(CH ₃) ₃	red
312	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-dibenzothiazol-2-ylthio	red
313	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-dibenzoxazol-2-ylthio	red
314	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diS-C \equiv N-N(CH ₃)CH \equiv N	red
315	2,6-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNH ₂ , 4,6-diOH	blue
316	2,6-di-O-C ₆ H ₄ -2-CO ₂ H	1,4,5,8-tetra NH ₂	blue
317	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-diNH ₂ , 2,6-diBr	blue
318	2,7-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNH ₂ , 4,5-diNHCO ₂ CH ₃	blue
319	2,7-di-SO ₂ -C ₆ H ₄ -2-CO ₂ H	1,8-diNH ₂ , 4,5-diOH	cyan
320	4,5-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNHCOCH ₃	orange
321	2,7-di-S-C ₆ H ₄ -2-CO ₂ H	1,8-diNH ₂ , 4,5-diNHC ₆ H ₅	cyan
322	2,6-di-O-C ₆ H ₄ -2-CO ₂ H	1,8-diNH ₂ , 4,5-diNHC ₆ H ₁₁	blue
323	2,8-di-SO ₂ -C ₆ H ₄ -4-CO ₂ H	1,4,5,8-tetra NH ₂	cyan
324	4,8-di-S-C ₆ H ₄ -2-CO ₂ H	1,5-NHCHCH ₂ SO ₂ CH ₂ CH	blue
325	2,3-di-O-C ₆ H ₄ -4-CO ₂ H	1,4-diNH ₂	violet
326	2,3-di-SO ₂ -C ₆ H ₄ -2-CO ₂ H	1,4-diNH ₂	blue

- 137 -

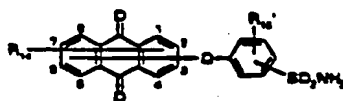
Table 12
Polydyes From Diacidic Anthraquinone Compounds of Formula XVI



Example No.		R ₁₂	Color
327		1,4-diOH	orange
328		1-di-NH ₂	violet
329		1-NH ₂ , 4-OH	red
330		1-NH ₂ , 4-NHC ₆ H ₅	violet
331		1-NH ₂ , 4-NHC ₆ H ₄ -4-Cl	blue
332		1-NH ₂ , 4-NHC ₆ H ₄ -4-OCH ₃	blue
333		1-NH ₂ , 4-NHSO ₂ C ₆ H ₄ -	red
334		1-NH ₂ , 4-C ₆ H ₄ -N ₂ O	red
335		1-NH ₂ , 2-SO ₂ -C ₆ H ₄	blue-green
336		1-NH ₂ , 2-Br	blue
337		1-NH ₂ , SO ₂ C ₆ H ₄ -3,4-diCl	blue

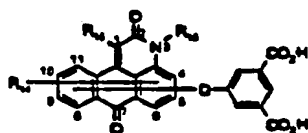
- 138 -

Table 12
Polydyes From Diacid Anthraquinone Compounds of Formula XVI



Example No.		R ₁	Color
338		1 - NH ₂ , 2 - CN	cyan
339		1 - NH ₂ , 2 - NO ₂	cyan
340		1 - NH ₂ , 2 - Br	blue
341		1 - NH ₂ , 2 - SO ₂ N(C ₂ H ₅) ₂	blue
342		1 - NH ₂ , 4 - NHC ₆ H ₄ , 3 - Cl	blue
343		1,8 - diOH, 5 - NO ₂	blue
344		1,5 - diOH, 8 - NH ₂	blue

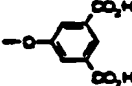
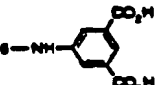
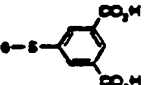
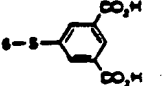
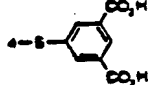
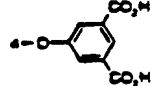
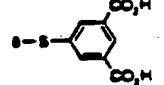
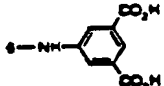
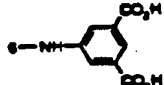
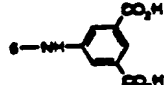
Table 13
Polydyes From Diacid Anthrapyridone Compounds of Formula XVIII



Example No.		R ₁₄	R ₁₂	R ₁₈	Color
345		H	CO ₂ C ₂ H ₅	CH ₃	red
346		H	CN	CH ₂ CH(CH ₃) ₂	violet
347		H	H	C ₆ H _{5-n}	red
348		H	Cl	C ₈ H ₁₁	red
349		H		CH ₃	red
350		H	CN	C ₆ H ₅	violet
351		H		CH ₃	violet
352		H	SO ₂ C ₆ H ₅	CH ₃	reddish blue

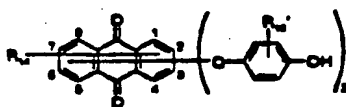
- 140 -

Table 13
 Polydyes From Diacidic Anthrapyridone Compounds of Formula XVIII

Example No.		R ₁₄	R ₁₅	R ₁₆	Color
353		4 - CH ₃	CO ₂ C ₂ H ₅	H	red
354		H	CO ₂ C ₂ H ₅	H	orange
355		H	CN	CH ₃	scarlet
356		6 - NHC ₆ H ₅	CN	CH ₃	violet
357		6 - NHC ₆ H ₅ - 4 - CH ₃	CO ₂ C ₂ H ₅	CH ₃	red
358		6 - NHC ₆ H ₅	H	CH ₃	red
359		H	COC ₆ H ₅	CH ₂ CH ₂ OC ₂ H ₅	red
360		H	CN	(CH ₂) ₇ CH ₃	violet
361		4 - Br	CN	CH ₃	violet

- 141 -

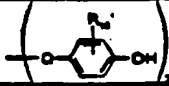
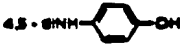
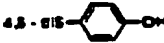



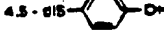
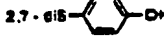
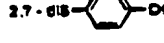
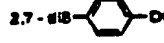

Table 14
Polydyes From Diacid Anthraquinone Compounds of Formula XIX



Example No.		R ₁₀	Color
362		H	red
363		H	red
364		H	red
365		H	red
366		1,4-diNH ₂	blue
367		1,8-diNHCH ₂ CH(CH ₃) ₂	blue
368		1,5-diSC ₆ H ₅	red
369			red
370			cyan
371			cyan
372		1,4-diNH ₂	violet

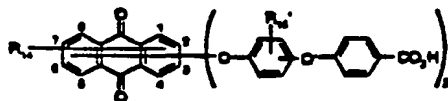
- 142 -

Table 14
Polydyes From Diacidic Anthraquinone Compounds of Formula XIX

Example No.		R ₂	Color
373		1,8-diOH	blue
374		1,8-diNHC ₆ H ₁₁	blue
375		1,8-diNHCH ₂ -  -CH ₂ OH	blue
376		1,8-diNHCH ₂ C(CH ₃) ₂ CH ₂ OH	blue
377		1,8-diNHCH ₂ CH(C ₂ H ₅)C ₆ H ₁₃	blue
378		1,4,5,8-tetra NH ₂	blue
379		1,8-diNH ₂ , 4,5-diOH	blue
380		1,8-diNH ₂ , 4,5-diNHC ₆ H ₅	cyan
381		H	yellow

- 143 -

Table 15
Polydyes From Diacid Anthraquinone Compounds of Formula XIXc



Example No.		R _M	Color
382		H	green
383		H	blue
384		H	blue
385		H	blue
386		H	blue
387		H	blue
388		1-NH ₂	red
389		1,4-diNH ₂	violet
390		1,4-diNH ₂	blue

- 144 -

Table 15
 Polydyes From Diacidic Anthraquinone Compounds of Formula XIXc

Example No.		R ₁₂	Color
391		H	red
392		H	red
393		H	red
394		H	red
395		H	red
396		H	red

- 145 -

Table 16
Polydyes From Diacidic Anthraquinone Compounds of Formula XIXd

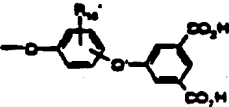
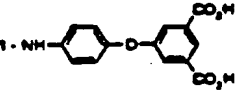
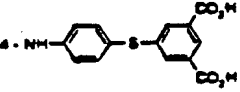
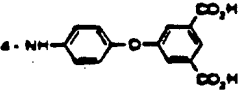
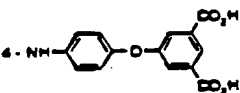
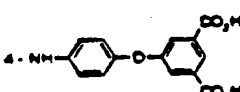
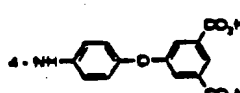
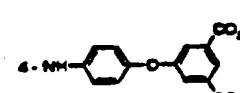
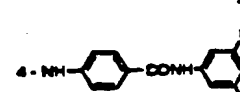
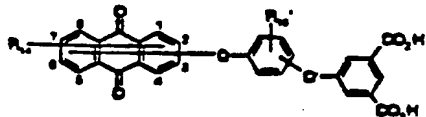
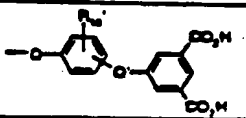
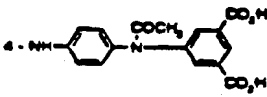
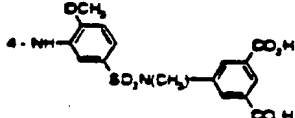
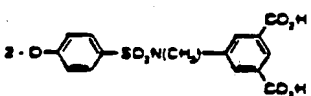
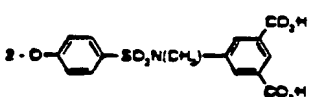
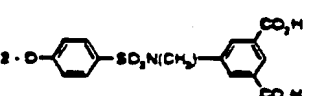
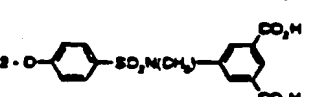
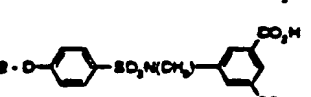
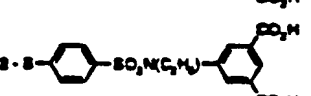
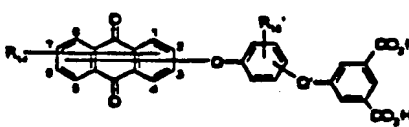
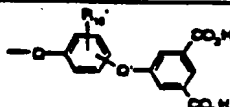
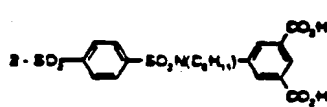
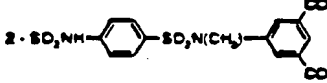
Example No.		R_{14}	Color
397		H	red
398		1-NHC ₆ H ₄ n	blue
399		1-NH ₂ , 2-CN	cyan
400		1-NH ₂ , 2-SO ₂ N(CH ₃)C ₆ H ₅	blue
401		1-NH ₂ , 2-CF ₃	cyan
402		1-NH ₂ , 2-S-C ₆ H ₄ -Cl	blue
403		1-NH ₂ , 2-OCH ₂ CH ₂ OH	violet
404		1-NH ₂ , 2-Br	blue

Table 16
Polydyes From Diacid Anthraquinone Compounds of Formula XIXd

			
Example No.		R ₁₄	Color
405		1-NH ₂ , 2-SO ₂ C ₆ H ₅	blue
406		1-NH ₂ , 2-Br	blue
407		1-NH ₂ , 4-OH	red
408		1,4-diNH ₂	violet
409		1-NH ₂ , 4-NH-C ₆ H ₄ -OCH ₃	violet
410		1-NH ₂ , 4-NH-SO ₂ -C ₆ H ₄ -CH ₃	red
411		1-NH ₂ , 4-S-C ₆ H ₄ -N	red
412		1-NH ₂ , 4-NHC ₆ H ₅	blue

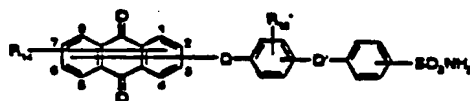
- 147 -

Table 16
 Polydyes From Diacid Anthraquinone Compounds of Formula XIXd

			
Example No.		R ₂	Color
413		1-NH ₂ , 4-NHC ₂ H ₅	blue
414		1-NH ₂ , 4-NHC ₂ H ₅	blue

- 148 -

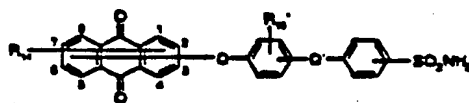
Table 17
Polydyes From Diacidic Anthraquinone Compounds of Formula XIXa



Example No.		R ₁	Color
415		H	red
416		1-NHCH ₃	blue
417		1-OH	violet
418		1-NH ₂ - 2-Br	blue
419		1-NH ₂ - 2-OC ₆ H ₅	violet
420		1-NH ₂ - 2-SO ₂ CH ₃	blue
421		1-NH ₂ - 2-COC ₆ H ₅	blue
422		1-NH ₂ - 2-CF ₃	cyan
423		1-NH ₂ - 2-CONH ₂	blue
424		1-NH ₂ - 2-SO ₂ N(CH ₃) ₂	blue
425		1-NHC ₆ H ₁₁	blue

- 149 -

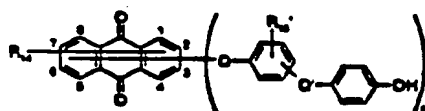
Table 17
Polydyes From Dicarboxylic Anthraquinone Compounds of Formula XIXa



Example No.		R ₁₄	Color
426		1-NHC ₆ H ₅	green
427		1-NH ₂ , 4-OH	red
428		1-NH ₂ , 4-NHSO ₂ CH ₃	red
429		1-NH ₂ , 4-NHCO ₂ C ₂ H ₅	red
430		1-NH ₂ , 4-NHSO ₂ C ₆ H ₅	red
431		1-NH ₂ , 4-NHCOC ₂ H ₅	red
432		1,4-diNH ₂	violet
433		1-NH ₂ , 4-NHC ₆ H ₅	blue
434		1,8-diOH, 5-NO ₂	blue
435		1-NH ₂ , 2-SO ₂ C ₆ H ₅	blue

- 150 -

Table 18
Polydyes From Diacidic Anthraquinones of Formula XIXI



Example No.		R ₁₄	Color
436		H	blue
437		H	blue
438		H	green
439		H	green
440		H	red
441		H	red
442		1,4-diNH ₂	violet
443		1,4-diNH ₂	blue
444		H	red

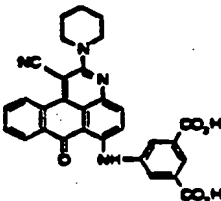
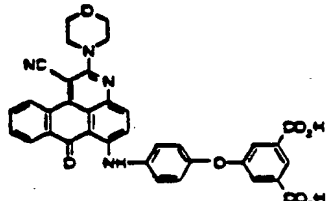
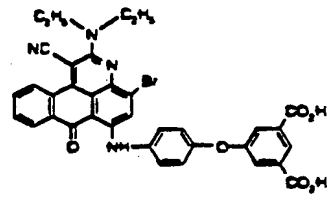
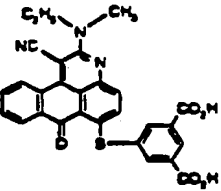
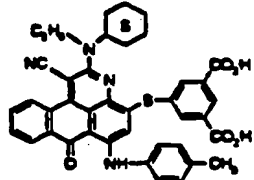
- 151 -

Table 18
Polydyes From Diacidic Anthraquinones of Formula XIX)

$ \begin{array}{c} \text{R}_1 \\ \\ \text{---} \text{Anthraquinone} \text{---} \text{R}_2 \\ \\ \text{R}_3 \end{array} \left(\text{---} \text{Ar} \text{---} \text{OH} \right)_n $		R ₄	Color
Example No.	$ \left(\text{---} \text{Ar} \text{---} \text{OH} \right)_n $		
445		4,8 - diNH ₂ , 3,7-diBr	blue
446		1 - NH ₂	red
447		6,7 - diCl	cyan
448		H	blue
449		H	blue

- 152 -

Table 19
Polydyes From Diacidic Anthrapyridines

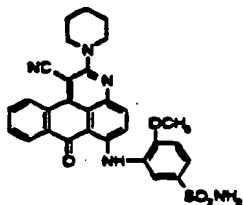
Example No.	Anthrapyridines	Color
450		red
451		bluish-red
452		red
453		orange
454		violet

- 153 -

Table 19
Polydyes From Diacidic Anthrapyridines

Example No.	Anthrapyridines	Color
-------------	-----------------	-------

455



red

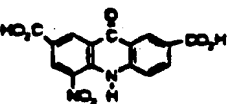
- 154 -

Table 20
Polydyes From Diacidic Nitroarylamines

Example No.	Nitroarylamine Compound	Color
456		yellow
457		yellow
458		yellow
459		yellow
460		yellow
461		yellow
462		yellow
463		yellow
464		yellow

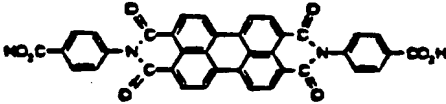
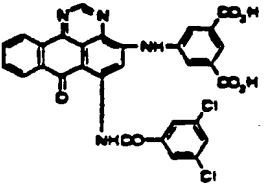
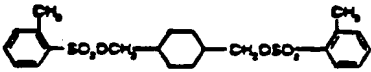
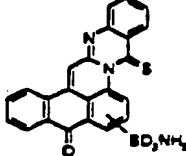
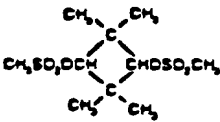
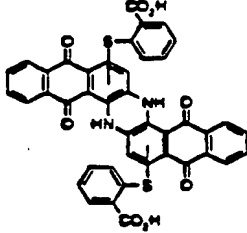
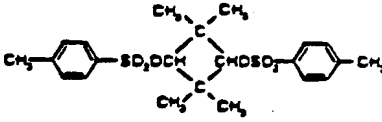
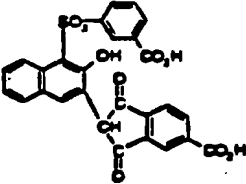
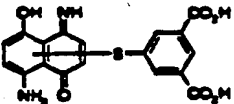
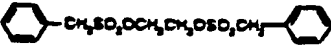
- 155 -

Table 20
Polydyes From Diacidic Nitroarylamines

Example No.	Nitroarylamine Compound	Color
485		yellow

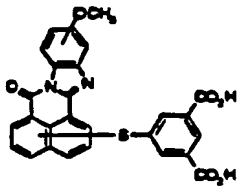
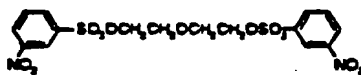
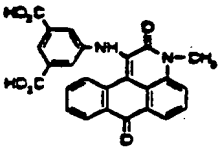
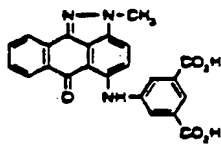
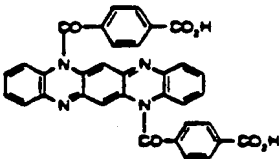
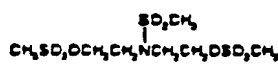
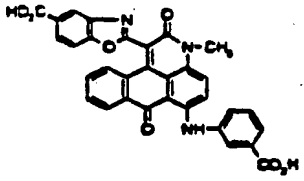
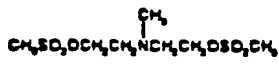
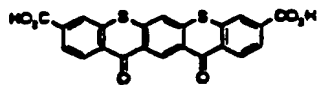

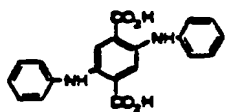
- 156 -

Table 21
Miscellaneous Polydyes

Example No.	Diacid Compound Reacted	Disulfonate Compound Reacted	Color
466		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_6\text{OSO}_2\text{CH}_3$	red
467			orange
468			yellow
469			blue
470		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	yellow
471			blue

- 157 -

Table 21
Miscellaneous Polydyes

Example No.	Diclidic Compound Reacted	Disulfonate Compound Reacted	Color
472			yellow
473		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SO}_2\text{CH}_3$	yellow
474		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	red
475			red
476			violet
477			yellow
478		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	orange

- 158 -

Table 21
Miscellaneous Polydyes

Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
479		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	orange
480		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OSO}_2\text{CH}_3$	yellow
481		$\text{CH}_3\text{CH}_2\text{SO}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OSO}_2\text{CH}_2\text{CH}_3$	red
482		$n\text{-C}_8\text{H}_{17}\text{SO}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OSO}_2\text{C}_8\text{H}_{17}$	yellow
483		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_6\text{OSO}_2\text{CH}_3$	red
484		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{---}(\text{CH}_2)_6\text{---}\text{CH}_2\text{OSO}_2\text{CH}_3$	orange
485		$\text{C}_6\text{H}_5\text{---SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	reddish-yellow

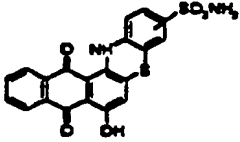
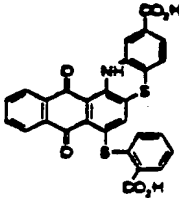
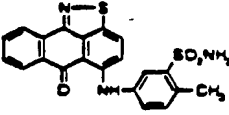
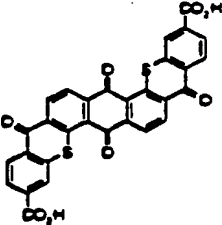
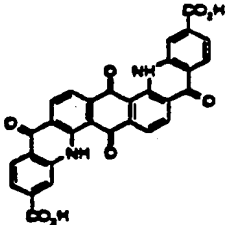
- 159 -

Table 21
Miscellaneous Polydyes

Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
486			yellow
487			blue
488			orange
489			yellow
490			yellow
491			yellow
492			blue

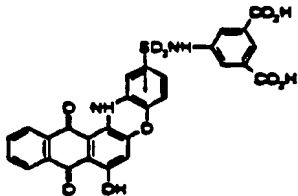
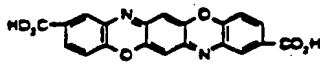
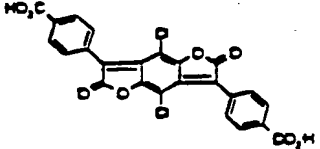
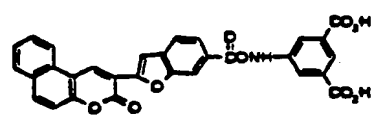
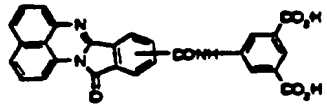
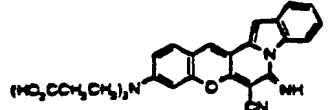
- 160 -

Table 21
Miscellaneous Polydyes

Example No.	Diacid Compound Reacted	Disulfonate Compound Reacted	Color
493		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{---}\text{C}_6\text{H}_4\text{---}\text{CH}_2\text{OSO}_2\text{CH}_3$	greenish-blue
494		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{---}\text{C}_6\text{H}_4\text{---}\text{SCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	greenish-blue
495		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{S---}\text{C}_6\text{H}_4\text{---}\text{SCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	red
496		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	orange
497		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_{10}\text{OSO}_2\text{CH}_3$	red

- 161 -

Table 21
Miscellaneous Polydyes

Example No.	Diacid Compound Reacted	Disulfonate Compound Reacted	Color
498		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{C}(\text{CH}_3)_2\text{OSO}_2\text{CH}_3$	blue
499		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	orange
500		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_6\text{OSO}_2\text{CH}_3$	red
501	$[\text{CuPc}] \text{SO}_2\text{NH}_2$ Pc = phthalocyanine	$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	blue
502	$[\text{CuPc}] \text{SO}_2\text{NH}-\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2$	$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	blue
503		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	yellow
504		$\text{CH}_3\text{SO}_2\text{OCH}_2-\text{C}_6\text{H}_{10}-\text{OCH}_2\text{OSO}_2\text{CH}_3$	reddish-yellow
505		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$	red

- 162 -

Table 22
Polymeric UV Absorbers

Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted
506		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_6\text{OSO}_2\text{CH}_3$
507		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
508		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OSO}_2\text{CH}_3$
509		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_6\text{OSO}_2\text{CH}_3$
510		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_6\text{OSO}_2\text{CH}_3$
511		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_6\text{OSO}_2\text{CH}_3$
512		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
513		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_6\text{OSO}_2\text{CH}_3$

- 163 -

Table 22
Polymeric UV Absorbers

Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted
S14		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_4\text{OSO}_2\text{CH}_3$
S15		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OSO}_2\text{CH}_3$
S16		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{SO}_2\text{CH}_3$
S17		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
S18		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
S19		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_6\text{OSO}_2\text{CH}_3$
S20		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OSO}_2\text{CH}_3$
S21		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OSO}_2\text{CH}_3$
S22		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OSO}_2\text{CH}_3$

- 164 -

Table 23
Polymeric Infrared Light Absorbers

Example No.	Diacid Compound Reacted	Disulfonate Compound Reacted
823		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
824		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_4\text{OSO}_2\text{CH}_3$
825		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_4\text{OSO}_2\text{CH}_3$
826		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_4\text{OSO}_2\text{CH}_3$
827		$\text{CH}_3\text{SO}_2\text{O}(\text{CH}_2)_4\text{OSO}_2\text{CH}_3$
828		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$

- 165 -

Table 23
Polymeric Infrared Light Absorbers

Example No.	Diacid Compound Reacted	Disulfonate Compound Reacted
529		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
530		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
531		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
532		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
533		$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
534	$[\text{PcAlOH}] \cdot \text{SO}_3\text{NH}_2$ Pc = phthalocyanine	$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$
535	$\text{NeS}(\text{OC}_6\text{H}_4)_2 \cdot \text{SO}_3\text{NH}_2$ Ne = naphthalene	$\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$

- 166 -

Table 23
Polymeric Infrared Light Absorbers

Example No.	Diacidic Compound Reacted	Dialkylsulfonate Compound Reacted
836	$\left[\text{PcAlOH} \right] \left(\text{CO}_2\text{M} \right)_2$ <p>Pc = phthalocyanine</p>	$\text{CH}_3\text{SO}_3\text{O}(\text{CH}_2)_8\text{OSO}_2\text{CH}_3$

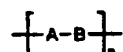
- 167 -

CLAIMS

WE CLAIM

1. A method comprising reacting
 - 5 a) at least one diacidic monomer, comprising about 1 to 100 mole % of at least one light-absorbing monomer having a light absorption maximum between about 300 nm and about 1200 nm and 99-0 mole % of a non-light absorbing monomer which does not absorb significant light
 - 10 at wavelengths above 300 nm or has a light absorption maximum below 300 nm, with
 - b) an organic compound having the formula
- X-B-X₁
- 15 wherein B is a divalent organic radical selected from the group consisting of C₂-C₁₂ alkylene, C₃-C₈ cycloalkylene, C₁-C₄ alkylene- C₃- C₈-cycloalkylene- C₁-C₄ alkylene, C₁-C₄ alkylene-arylene- C₁-C₄ alkylene, C₂- C₄-alkylene-L-
 - 20 arylene-L- C₂-C₄ alkylene and C₂-C₄ alkylene-(L- C₂-C₄ alkylene)₁₋₄, wherein L is a linking group selected from the group consisting of -O-, -S-, -SO₂-, -NH-, -N(C₁-C₆ alkyl)-, -N(aryl)-, -N(SO₂ C₁-C₆ alkyl)-, -N(SO₂aryl)-, -SO₂N(C₁-C₆ alkyl)- and combinations thereof; X and X₁ are
 - 25 reactive groups and are independently selected from the group consisting of bromine, iodine and R-SO₂O; wherein R is selected from the group consisting of C₁-C₆ alkyl; C₁-C₆ alkyl substituted with chlorine, fluorine, C₁-C₆ alkoxy, aryl, aryloxy, arylthio or C₃-C₈ cycloalkyl; C₃-C₈
 - 30 cycloalkyl or aryl,
- wherein said reaction is carried out in a solvent in the presence of a base to form a light absorbing polymeric composition having the formula

- 168 -



wherein B is as defined above, n is at least 2 and A comprises the residue of said diacidic monomer.

5

2. The process of claim 1 where said light-absorbing monomers have the formula



10

wherein H represents an acidic hydrogen atom; Y is a divalent light-absorbing moiety selected from the group consisting of chromophoric classes of azo, disazo, triazo, bis-azo, methine, arylidene, polymethine, azo-methine, azamethine, anthraquinone, anthrapyridone (3H-dibenz[f,i]isoquinoline-2,7-dione, nitroarylamines anthrapyridine (7H-dibenz[f,i]isoquinoline-7-one, phthaloylphenothiazine (14H-naphth[2,3-a]phenothiazine-8,13-dione, benzanthrone (7H(de)anthracene-7-one), anthrapyrimidine (7H-benzo[e]perimidine-7-one), anthrapyrazole, anthraisothiazole, triphenodioxazine, thiaxanthene-9-one, fluorindine (5,12-dihydroquinoxaline [2,3-b]phenazine, quinophthalone, phthalocyanine, metal phthalocyanine, naphthalocyanine, metal naphthalocyanine, nickel dithiolenes, squarylium compounds, croconium compounds, coumarin (2H-1-benzopyran-2-one), coumarin imine (2H-1-benzopyran-2-imine), perinone, benzodifuran, phthaloylacridone, phthaloylphenoxazine (14H-naphtho[2,3-a]phenoxazine-8,13-dione, phthaloylacridone (13H-naphtho[2,3-c] acridine-5,8,14-trione), anthraquinonethioxanthene (8H-naphtho[2,3-c]thioxanthene-5,8,13-trione, anthrapyridazone, pyrrolo[3,4-c]pyrrole, indigo, thioindigo, quinoline, xanthene, acridine, azine, cyanine, oxazine, 1,4 and 1,5-naphthoquinones, 2,5-

15

20

25

30

- 169 -

diarylamino-terephthalic acids and esters, pyromellitic acid diimide, naphthalene-1,4,5,8-tetracarboxylic acid diimide, 3,4,9,10-perylenetetracarboxylic acid diimide, 3-aryl-2,5-dioxypyrroline, 3-aryl-5-dicyanomethylene-2-oxopyrroline, arylisoindoline, hydroxybenzophenone, benotriazole, naphthotriazole, diminoisoindoline, naphthopyran (3H-naphtho[2,1-6]pyran-3-one and 3-imine, phthalimides, 2-arylbenzazoles, carbostyryls, 1,2-diarylethenes, 2,5-diarylthiophenes, 2,5-diaryl-1,3,4-oxadiazoles, triazines, 2,5-diarylfurans, 2,5-diaryl-1,3,4-thiadiazoles, thiophenes, 1,3-diphenyl-2-pyrazolines, 2-arylbenzofurans, 2,6-diphenylbenzofurans, quinolines, quinoxalines, 3,4-diarylfuranones, distyrylarenes, benzanthrones, polyarenes and naphthalimides.

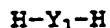
3. The method of claim 2 wherein the hydrogen atoms of said formula H-Y-H are independently bonded to an oxygen, sulfur, or nitrogen atom which is a part of the light absorbing moiety Y and which in combination provides two acidic functional groups.

4. The method of claim 3 wherein said acidic functional groups have pKa values of from about 1.5 to about 12.

5. The method of claim 3 wherein said acidic functional groups are independently selected from the group consisting of -CO₂H, -SH, -OH attached to an aromatic ring, -CONHCO-, -SO₂-NH-CO-, -SO₂-NH-SO₂-, 1(H)-1,2,4-triazol-3-yl-, imidazolyl, benzimidazolyl, pyrazolyl, -SO₂H attached to aromatic ring, -NHSO₂R₃ and -SO₂NHR₃, wherein R₃ is selected from the group consisting of C₁-C₆ alkyl, C₃-C₈ cycloalkyl, aryl and C₁-C₆ alkyl substituted with at least one group selected from the group consisting of C₁-C₆ alkoxy, aryl, aryloxy, arylthio and C₃-C₈ cycloalkyl.

6. The method of claim 1 wherein said non light-absorbing monomers have the formula

- 170 -

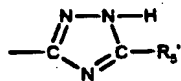


wherein H represents an acidic hydrogen atom; Y₁ is a
 5 divalent moiety selected from the group consisting of -O₂C-
 R₁-CO₂- and -O-R₂-O- and -O₂C-R₃-O-, wherein R₁ is selected
 from the group consisting of C₂-C₁₂ alkylene, 1-4-
 cyclohexylene, arylene, arylene-O-arylene, arylene-SO₂-
 arylene, arylene-S-arylene, and C₁-C₄ alkylene-O- C₁-C₄
 10 alkylene; wherein R₂ is selected from the group consisting
 of arylene, arylene-O-arylene, arylene-S-arylene, arylene-
 SO₂-arylene, phenylene-phenylene, and phenylene-C(R₄)₂-
 phenylene; wherein R₄ is selected from the group
 consisting of hydrogen and C₁-C₄ alkyl; wherein R₃ is
 15 selected from arylene.

7. The method of claim 1 wherein said polymeric
 composition is linear.

8. The method of claim 1 wherein said diacidic
 monomers have pK_a values of about 12 or below.

20 9. The method of claim 2 wherein H-Y-H includes a
 moiety selected from the group consisting of carboxy
 groups attached to an aromatic ring carbon or aliphatic
 carbon, hydroxy groups attached to an unsubstituted or
 substituted phenyl or naphthyl radical, -CO-NHCO- groups
 25 attached to an aromatic ring to provide an imide and
 1(H)-1,2,4-triazol-3-yl group having the formula



30 wherein R₅' is selected from the group consisting of
 hydrogen, C₁-C₆ alkyl and aryl.

10. The method of claim 1 where n is between about
 2 and about 25.

- 171 -

11. The method of claim 1 wherein n is between about 3 and about 15.

12. The method of claim 1 wherein said base is selected from the group consisting of alkali metal
5 carbonates, alkali metal bicarbonates and tertiary amines, aromatic nitrogen bases, bicyclic nitrogen containing bases having non-hindered electron pairs and mixtures thereof.

13. The method of claim 12 wherein said base is
10 selected from the group consisting of triethylamine, tri-n-butylamine, N-methylpiperidine, N,N'-dimethylpiperazine, N-methylmorpholine and N,N,N',N'-tetramethylethylenediamine, pyridines, picolines, quinolines, isoquinolines, N-alkylpyrroles, N-
15 alkylimidazoles, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), 1,5-diazabicyclo[4,3,0]non-5-ene (DBN) and 1,4-diazadicyclo[2,2,2]octane (DABCO®) and mixtures thereof.

14. The method of claim 1 wherein said solvent is one or more aprotic polar solvents.

15. The method of claim 1 wherein said solvent is
20 selected from the group consisting of N,N-dimethylacetamide, N,N-dimethylformamide, N-methyl-2-pyrrolidone, N-methyl-N-phenyl formamide, dimethylsulfoxide, aliphatic nitriles, sulfolane, hexamethyl phosphoramidate, water, alcohols, ketones
25 pyridine and ether-alcohols and mixtures thereof.

16. The method of claim 15 wherein said solvent is selected from the group consisting of N,N-dimethylacetamide, N,N-dimethylformamide, N-methyl-2-
30 pyrrolidone, N-methyl-N-phenyl formamide, dimethylsulfoxide, aliphatic nitriles, sulfolane and hexamethyl phosphoramidate and mixtures thereof.

17. The method of claim 1 wherein said reacting is conducted at a temperature between about 75°C and about
35 125°C.

- 172 -

18. The method of claim 1 wherein said organic compound having the formula



5 is selected from the group consisting of disulfonate compounds where X and X₁ are both a sulfonate ester of the formula-OSO₂R, wherein R is selected from C₁-C₄ alkyl, phenyl or p-methylphenyl and wherein B is selected from
10 C₂-C₆ alkylene, -CH₂-1,4-cyclohexylene-CH₂-, -CH₂CH₂(OCH₂CH₂)₁₋₄ and -CH₂CH₂O-1,4-phenylene-O-CH₂CH₂-.

19. The method of claim 18 wherein said B moiety of organic compound of Formula II is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)CH₂-, -CH₂C(CH₃)₂CH₂-,
15 -(CH₂)₄-, -(CH₂)₆-, -CH₂CH₂OCH₂CH₂- and -CH₂-1,4-cyclohexylene-CH₂-.

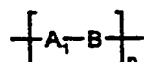
20. The method of claim 1 wherein said organic compound having the formula X-B-X₁ is selected from the group consisting of 1,2-ethandiol, dimethanesulfonate;
20 1,2-ethanediol bis(4-methylbenzenesulfonate); 1,4-butanediol, dimethane sulfonate; 1,6-hexanediol, dimethanesulfonate; 1,3-propanediol, 2,2-dimethyl-, dimethanesulfonate; 1,4-cyclohexanedimethanol, dimethanesulfonate; 1,1,3,3-tetramethylcyclobutanediol,
25 dimethanesulfonate, and ethanol 2,2'-oxybis-dimethanesulfonate.

21. The method of claim 1 wherein A of said light absorbing polymeric composition comprises 100 mole% of said light-absorbing monomer.

30 22. The method of claim 1 wherein said diacidic light absorbing monomer has a light absorption maximum between about 300 nm and about 1200 nm and is present in said light absorbing polymeric composition in an amount at least about 50% by weight %.

35 23. A light absorbing composition having the formula

- 173 -



- wherein A₁ comprises the residue of at least one diacidic monomer having a light absorption maximum between about 300 nm and about 1200 nm, and wherein B is a divalent organic radical selected from the group consisting of C₂-C₁₂ alkylene, C₃-C₈ cycloalkylene, C₁-C₄ alkylene- C₃-C₈-cycloalkylene- C₁-C₄ alkylene, C₁-C₄ alkylene-arylene- C₁-C₄ alkylene, and C₂- C₄-alkylene-L-arylene-L- C₂-C₄ alkylene and C₂-C₄ alkylene-(L- C₂-C₄ alkylene)₁₋₄, wherein L is a linking group selected from-O-, -S-, -SO₂-, -NH-, -N(C₁-C₆ alkyl)-, -N(aryl)-, -N(SO₂ C₁-C₆ alkyl)-, -N(SO₂aryl)-, -SO₂N(C₁-C₆ alkyl)- and combinations thereof; wherein n is at least 2.

24. A composition comprising a thermoplastic polymer blended with at least one light absorbing linear polymeric composition of claim 23.

25. The composition of claim 24 wherein said thermoplastic polymer is selected from the group consisting of polyesters, polyolefins, polyamides, polyimides, polyvinyl chloride, polyurethanes, polycarbonates, cellulose esters, polyacrylates, polyvinylesters, polyester-amides, polystyrene, polyacrylonitrile-butadiene- styrene, polystyrene-acrylonitrile and mixtures and blends thereof.

26. The composition of claim 23 wherein A₁ comprises the residue of at least one diacidic monomer having the structure



- wherein H represents an acidic hydrogen atom and Y is a divalent light-absorbing moiety selected from the chromophoric classes consisting of azo, disazo, triazo, bis-azo, methine, arylidene, polymethine, azo-methine, azamethine, anthraquinone, anthrapyridone (3H-dibenz[f,i,j] isoquinoline-2,7-dione, nitroarylamines anthrapyridine

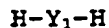
- 174 -

- (7H-dibenz[f,ij]isoquinoline-7-one, phthaloylphenothiazine (14H-naphth[2,3-a]phenothiazine-8,13-dione, benzanthrone (7H(de)anthracene-7-one), anthrapyrimidine (7H-benzo[e]perimidine-7-one), anthrapyrazole,
- 5 anthraisothiazole, triphenodioxazine, thiaxanthene-9-one, fluorindine (5,12-dihydroquinoxaline [2,3-b]phenazine, quinophthalone, phthalocyanine, metal phthalocyanine, naphthalocyanine, metal naphthalocyanine, nickel dithiolenes, squarylium compounds, croconium compounds,
- 10 coumarin (2H-1-benzopyran-2-one), coumarin imine (2H-1-benzopyran-2-imine), perinone, benzodifuran, phthaloylacridone, phthaloylphenoxazine (14H-naphtho[2,3-a]phenoxazine-8,13-dione, phthaloylacridone (13H-naphtho[2,3-c] acridine-5,8,14-trione),
- 15 anthraquinonethioxanthane (8H-naphtho[2,3-c]thioxanthene-5,8,13-trione, anthrapyridazone, pyrrolo[3,4-c]pyrrole, indigo, thioindigo, quinoline, xanthene, acridine, azine, cyanines, oxazine, 1,4 and 1,5-naphthoquinones, 2,5-diarylamino-terephthalic acids and esters, pyromellitic
- 20 acid diimide, naphthalene-1,4,5,8-tetracarboxylic acid diimide, 3,4,9,10-perylenetetracarboxylic acid diimide, 3-aryl-2,5-dioxypyrroline, 3-aryl-5-dicyanomethylene-2-oxopyrroline, arylisoindoline, hydroxybenzophenone, benotriazole, naphthotriazole, diminoisoindoline,
- 25 naphthopyran (3H-naphtho[2,1-6]pyran-3-one and 3-imine, phthalimides, 2-arylbenzazoles, carbostyryls, 1,2-diarylethenes, 2,5-diarylthiophenes, 2,5-diaryl-1,3,4-oxadiazoles, triazines, 2,5-diarylfurans, 2,5-diaryl-1,3,4-thiadiazoles, thiophenes, 1,3-diphenyl-2-
- 30 pyrazolines, 2-arylbenzofurans, 2,6-diphenylbenzofurans, quinolines, quinoxalines, 3,4-diarylfuranones, distyrylarenes, benzanthrone, polyarenes and naphthalimides.

27. The light absorbing linear polymeric
- 35 composition of claim 23 or 26

- 175 -

wherein A₁ further comprises less than about 50% by weight of the total composition of a residue of at least one non-light absorbing monomer having the formula



5

wherein Y₁ is a divalent moiety, selected from the group consisting of -O₂C-R₁-CO₂- and -O-R₂-O- and -O₂C-R₃-O-, wherein R₁ is selected from the group consisting of C₂-C₁₂ alkylene, 1-4-cyclohexylene, arylene, arylene-O-arylene, arylene-SO₂-arylene, arylene-S-arylene, and C₁-C₄ alkylene-O-C₁-C₄ alkylene; wherein R₂ is selected from the group consisting of arylene, arylene-O-arylene, arylene-S-arylene, arylene-SO₂-arylene, phenylene-phenylene, and phenylene-C(R₄)₂-phenylene; wherein R₄ is selected from the group consisting of hydrogen and C₁-C₄ alkyl; wherein R₃ is arylene; wherein B is a divalent organic radical selected from the group consisting of C₂-C₁₂ alkylene, C₃-C₈ cycloalkylene, C₁-C₄ alkylene-C₃-C₈-cycloalkylene-C₁-C₄ alkylene, C₁-C₄ alkylene-arylene-C₁-C₄ alkylene, and C₂-C₄-alkylene-L-arylene-L-C₂-C₄ alkylene and C₂-C₄ alkylene-(L-C₂-C₄ alkylene)₁₋₄, wherein L is a linking group selected from -O-, -S-, -SO₂-, -NH-, -N(C₁-C₆ alkyl)-, -N(aryl)-, -N(SO₂ C₁-C₆ alkyl)-, -N(SO₂aryl)-, -SO₂N(C₁-C₆ alkyl)- and combinations thereof; wherein n is at least 2.

25

28. The light absorbing linear polymeric composition of Claim 25 wherein A₁ comprises the residue of at least one diacidic monomer having at least one acidic group other than carboxy and having a light absorption maximum between about 300 nm and about 1200 nm and wherein B is a divalent organic radical selected from C₂-C₁₂ alkylene, C₃-C₈ cycloalkylene, C₁-C₄ alkylene-C₃-C₈-cycloalkylene-C₁-C₄ alkylene, C₁-C₄ alkylene-arylene-C₁-C₄ alkylene, and C₂-C₄-alkylene-L-arylene-L-C₂-C₄ alkylene and C₂-C₄ alkylene-(L-C₂-C₄ alkylene)₁₋₄, wherein L is a linking group selected from -O-, -S-, -SO₂-, -NH-, -N(C₁-C₆ alkyl)-, -N(aryl)-, -N(SO₂ C₁-C₆ alkyl)-,

30

35

- 176 -

-(SO₂aryl)-, -SO₂N(C₁-C₆ alkyl)- and combinations thereof; wherein n is at least 2.

29. The process of claim 2 wherein said light absorbing monomer comprises two carboxy groups as acidic functional groups.

30. The process of claim 2 wherein said light absorbing monomer comprises two 1(H)-1,2,4-triazol-3-ylthio groups as acidic functional groups.

31. The process of claim 2 wherein said light absorbing monomer comprises one carboxy and one 1(H)-1,2,4-triazol-3-ylthio group as acidic functional groups.

32. The process of claim 2 wherein said light absorbing monomer comprises two hydroxy groups attached to aromatic ring(s).

33. The process of claim 2 wherein said light absorbing monomer comprises one imide group and one carboxy group.

34. The process of claim 2 wherein said light absorbing monomer comprises one imide group and one 1(H)-1,2,4-triazol-3-ylthio group.

35. The composition of claim 25 wherein said light absorbing monomer comprises two carboxy groups as acidic functional groups.

36. The composition of claim 25 wherein said light absorbing monomer comprises two 1(H)-1,2,4-triazol-3-ylthio groups as acidic functional groups.

37. The composition of claim 25 wherein said light absorbing monomer comprises one carboxy and one 1(H)-1,2,4-triazol-3-ylthio group as acidic functional groups.

38. The composition of claim 25 wherein said light absorbing monomer comprises two hydroxy groups attached to aromatic ring(s).

39. The composition of claim 25 wherein said light absorbing monomer comprises one imide group and one carboxy group.

- 177 -

40. The composition of claim 23 wherein said light absorbing monomer comprises one imide group and one 1(H)-1,2,4-triazol-3-ylthio group.

41. The composition of claim 23 wherein said light
5 absorbing monomer comprises a diacidic sulfamoyl ($-\text{SO}_2\text{NH}_2$) group.

42. The composition of claim 25 wherein said light absorbing monomer comprises two acidic groups independently selected from the group consisting of $-\text{CO}_2\text{H}$,
10 SH , hydroxy attached to an aromatic ring, $-\text{CONHCO}-$ (imide), $-\text{SO}_2\text{NHCO}-$, $-\text{SO}_2\text{NHSO}_2-$, 1(H)-1,2,4-triazolyl-3-yl-, imidazolyl, benzimidazolyl, pyrazolyl, $-\text{SO}_2\text{H}$ attached to an aromatic ring, $-\text{NHSO}_2\text{R}_5$ and $-\text{SO}_2\text{NHR}_5$, wherein R_5 is selected from the group consisting of C_1-C_6 alkyl; C_1-C_6
15 alkyl substituted with at least one group selected from C_1-C_6 alkoxy, aryl, aryloxy, arylthio and C_3-C_8 cycloalkyl; C_3-C_8 cycloalkyl; aryl.

43. The composition of claim 27 wherein said light absorbing monomer comprises two carboxy groups as acidic
20 functional groups.

44. The composition of claim 27 wherein said light absorbing monomer comprises two 1(H)-1,2,4-triazol-3-ylthio groups as acidic functional groups.

45. The composition of claim 27 wherein said light
25 absorbing monomer comprises one carboxy and one 1(H)-1,2,4-triazol-3-ylthio group as acidic functional groups.

46. The composition of claim 27 wherein said light absorbing monomer comprises two hydroxy groups attached to aromatic ring(s).

47. The composition of claim 27 wherein said light
30 absorbing monomer comprises one imide group and one carboxy group.

48. The composition of claim 27 wherein said light
35 absorbing monomer comprises one imide group and one 1(H)-1,2,4-triazol-3-ylthio group.

- 178 -

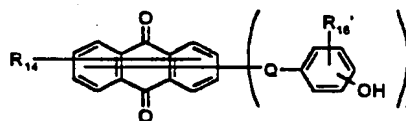
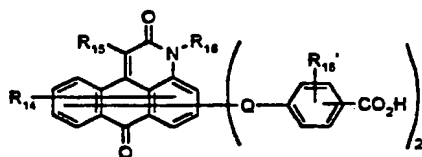
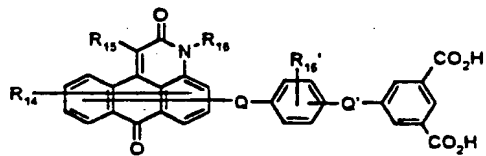
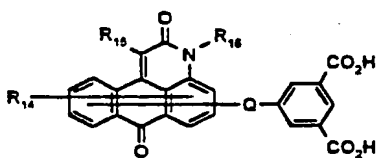
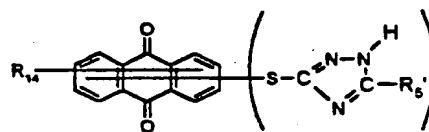
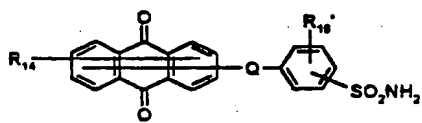
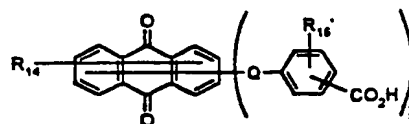
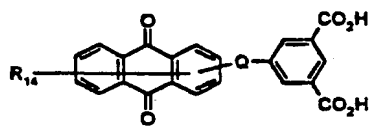
49. The composition of claim 27 wherein said light absorbing monomer comprises a diacidic sulfamoyl ($-\text{SO}_2\text{NH}_2$) group.

50. The composition of claim 27 wherein said light
5 absorbing monomer comprises two acidic groups independently selected from $-\text{CO}_2\text{H}$, SH , hydroxy attached to an aromatic ring, $-\text{CONHCO}-$ (imide), $-\text{SO}_2\text{NHCO}-$, $-\text{SO}_2\text{NHSO}_2-$, 1(H)-1,2,4-triazolyl-3-yl-, imidazolyl, benzimidazolyl, pyrazolyl, $-\text{SO}_2\text{H}$ attached to an aromatic ring, $-\text{NHSO}_2\text{R}_3$
10 and $-\text{SO}_2\text{NHR}_3$, wherein R_3 is selected from C_1-C_6 alkyl; C_1-C_6 alkyl substituted with at least one group selected from C_1-C_6 alkoxy, aryl, aryloxy, arylthio and C_3-C_8 cycloalkyl; C_3-C_8 cycloalkyl; aryl.

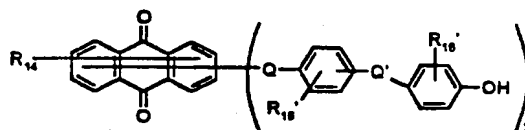
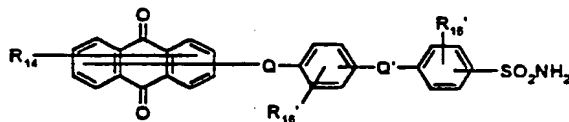
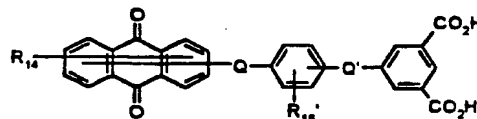
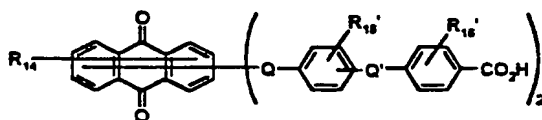
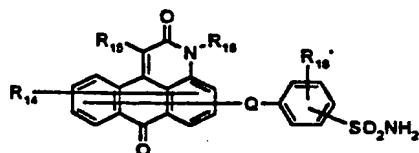
51. The light absorbing linear polymeric composition
15 of claim 27 wherein said at least one diacidic monomer comprises at least about 50% by weight of the total composition.

52. The composition of claim 51 wherein the light
20 absorbing portion of A comprises the residue of at least one diacidic light absorbing monomer selected from the group consisting of the anthraquinone and anthrapyridone colorants having the structures:

- 179 -

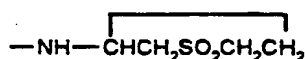


- 180 -

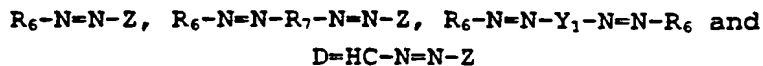


- wherein R_{14} is selected from the group consisting of hydrogen and 1-4 groups selected from amino, C_1 - C_{10}
- 5 alkylamino, C_3 - C_8 alkenylamino, C_3 - C_8 alkynylamino, C_3 - C_8 cycloalkylamino, arylamino, halogen, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, aryl, aroyl, C_1 - C_6 alkanoyl, C_1 - C_6 alkanoyloxy, NHCO C_1 - C_6 alkyl, NHCOaryl, NHCO₂ C_1 - C_6 alkyl, NHSO₂ C_1 - C_6 alkyl, NHSO₂ aryl, C_1 - C_6 alkoxy carbonyl, aryloxy, arylthio,
 - 10 heteroarylthio, cyano, nitro, trifluoromethyl, thiocyno, SO₂ C_1 - C_6 alkyl, SO₂ aryl, -SO₂NH C_1 - C_6 alkyl, -SO₂N(C_1 - C_6 alkyl)₂, -SO₂N(C_1 - C_6 alkyl) aryl, CONH C_1 - C_6 alkyl, CON(C_1 - C_6 alkyl)₂, CON(C_1 - C_6 alkyl) aryl, C_1 - C_6 alkyl, furfurylamino, tetrahydrofurfurylamino, 4-(hydroxymethyl)
 - 15 cyclohexanemethylamino,

- 181 -



- or hydroxy; Q and Q' are independently selected from the group consisting of -O-, -N(COR₁₀)-, -N(SO₂R₁₀)-, -N(R₁₀)-, -S-, -SO₂-, -CO₂-, -CON(R₁₀)-, SO₂N(R₁₀)-, wherein R₁₀ is selected from the group consisting of hydrogen, aryl, C₃-C₈ cycloalkyl, or C₁-C₁₀ alkyl; R₁₅ is selected from the group consisting of hydrogen, cyano, C₁-C₆ alkylamino, C₁-C₆ alkoxy, halogen, arylthio, aryl, heteroaryl, heteroarylthio, C₁-C₆ alkoxycarbonyl, aroyl or arylsulfonyl; R₁₆ is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₃-C₈ cycloalkyl and aryl; R₁₆' is selected from the group consisting of hydrogen, C₁-C₆ alkyl, halogen and C₁-C₆ alkoxy; wherein each C₁-C₆ alkyl group and C₁-C₆ alkyl group which is a portion of another group may contain at least one substituent selected from the group consisting of hydroxy, cyano, chlorine, fluorine, C₁-C₆ alkoxy, C₃-C₈ cycloalkoxy, C₁-C₆ alkylcyclohexyl, hydroxymethyl cyclohexyl, aryl and heteroaryl; with the provision that two acidic groups containing one acidic proton each or one acidic group containing two acidic hydrogens be present in the diacidic compounds.
53. The composition of claim 26 or 27 wherein the light absorbing portion of A comprises the residue of at least one light absorbing monomer selected from the group consisting of azo, disazo, bis-azo and azomethine and having respectively the structures:



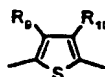
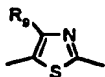
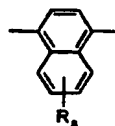
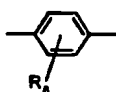
- wherein R₆ is the residue of an aromatic or heteroaromatic amine which has been diazotized and coupled with a coupling component H-Z and is derived from an amine

- 182 -

- selected from the group consisting of aromatic and heteroaromatic amine classes selected from the group consisting of aniline, 1-aminonaphthalene, 1-aminoanthraquinone, 4-aminoazobenzene, 2-aminothiazole, 2-aminobenzothiazole, 3-amino-2,1-benzisothiazole, 2-aminothieno[2,3-d]thiazole, 5-aminoisothiazole, 5-aminopyrazole, 4-aminopyrazoloisothiazole, 2-amino-1,3,4-thiadiazole, 5-amino-1,2,4-thiadiazole, 5-amino-1,2,3-triazole, 2-amino-1,3,4-triazole, 2(5) aminoimidazole, 3-aminopyridine, 2(3) aminothiophene, 2(3) aminobenzo[b]thiophene, 2-aminothieno[3,2-b]thiophene, 3-aminothieno[2,3-c]isothiazole, 3-amino-7-benz-2,1-isothiazole, 3-aminobenzothienoisothiazole, 3-aminoisothiazole[3,4-d]pyrimidine, 5-amino-1,2,3-triazole, 3(4) aminophthalimide and 5(6) amino-1,2-benzisothiazolon-1,1-dioxide with said aromatic and heteroaromatic ring systems being unsubstituted or substituted with one or more groups selected from C₁-C₁₀ alkyl, C₁-C₆ alkoxy, C₃-C₈ cycloalkyl, carboxy, halogen, C₁-C₆ alkoxycarbonyl, formyl, C₁-C₆ alkanoyl, C₁-C₆ alkanoyloxy, dicyanovinyl, C₃-C₈-cycloalkanoyl, thiocyano, trifluoroacetyl, cyano, carbamoyl, -CONH-C₁-C₆ alkyl, CONHaryl, CON(C₁-C₆ alkyl)₂, sulfamoyl, SO₂NH C₁-C₆ alkyl, SO₂N(C₁-C₆ alkyl)₂, SO₂NHaryl, SO₂NH C₃-C₈ cycloalkyl, CONH C₃-C₈ cycloalkyl, aryl, aroyl, -NHSO₂ C₁-C₆ alkyl, -N(C₁-C₆ alkyl)SO₂ C₁-C₆ alkyl, -NHSO₂ aryl, NHCO C₁-C₆ alkyl, NHCO C₃-C₈ cycloalkyl, NHCOaryl, NHCO₂ C₁-C₆ alkyl, NHCONH C₁-C₆ alkyl, NHCONHaryl, N(C₁-C₆ alkyl)aryl, arylazo, heteroaryl, aryloxy, arylthio, C₃-C₈ cycloalkoxy, heteroarylazo, heteroarylthio, arylsulfonyl, tricyanovinyl, aryloxysulfonyl, C₁-C₆ alkylsulfonyl, trifluoromethyl, fluorosulfonyl, trifluoromethylsulfonyl, thiocyano, hydroxy, nitro or CH=D, wherein D is the residue of an active methylene compound selected from the group consisting of malononitrile, α-cyanoacetic acid esters, malonic acid esters, α-cyanacetic acid amides, α-C₁-C₆

- 183 -

- alkylsulfonylacetonitriles, α -arylsulfonylacetonitriles, α -C₁-C₆ alkanoylacetonitriles, α -aroylacetonitriles, α -heteroarylacetonitriles, bis(heteroaryl)methanes, 1,3-indanediones, 2-furanones, benzo-2-furanones, naphtho-2-furanones, 2-indolones, 3-cyano-1,6-dihydro-4-methyl-2,6-dioxy (2H)-pyridines, benzo (b) thieno-3-ylidene propane dinitrile-5,5-dioxides, 1,3-bis(dicyanomethylene) indanes, barbituric acid, 5-pyrazolones, dimedone, 3-oxo-2,3-dihydro-1-benzothiophene-1,1-dioxides or aryl-C(CH₃)C=C(CN)₂; wherein R₇ is a divalent aromatic or heteroaromatic radical selected from the group consisting of 1,4-phenylene, naphthalene-1,4-diyl, thiazol-2,5-diyl and thiophene-2,5-diyl:



15

- wherein R₈ is selected from the group consisting of hydrogen or 1-2 groups selected from C₁-C₆ alkyl, C₁-C₆ alkoxy, cyano, halogen, -NHCO C₁-C₆ alkyl, -NHCO₂ C₁-C₆ alkyl, -NHCO aryl, -NHCONH aryl or NHCONH C₁-C₆ alkyl; R₉ is selected from the group consisting of hydrogen, C₁-C₆ alkyl, halogen, aryl, heteroaryl; R₁₀ is selected from the group consisting of hydrogen, C₁-C₆ alkoxy, carbonyl, cyano, carbamoyl, aryl, arylsulfonyl, aroyl, -CONH C₁-C₆ alkyl, or C₁-C₆ alkylsulfonyl; wherein Z is the residue of a coupling compound selected from the group consisting of electron rich compound classes of anilines, 1-aminonaphthalenes, 1,2-dihydroquinolines, 1,2,3,4-tetrahydroquinolines, benzomorpholines (3,4-dihydro-2H-1,4-benzoxazine),

20

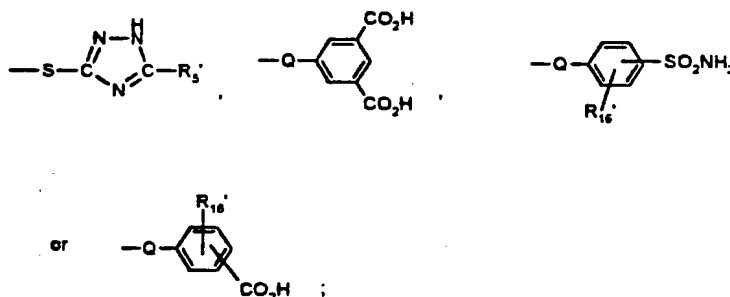
25

- 184 -

- pyrazolones, pyrazoles, 3-cyano-6-hydroxy-2-pyridones, 2,3-dihydroindoles, indoles, 4-hydroxycoumarins, 4-hydroxy-2-quinolones, imidazo[2,1-b]thiazoles, julolidines (2,3,6,7-tetrahydro-1H,5H-
- 5 benzo[ij]quinolizines), 1-oxajulolidines, 1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolines, 2,6-diamino-3 cyanopyridines, 2-aminothiazoles, 2-aminothiophenes, 5,5-dimethyl-1,3-cyclohexanedione (dimedone), phenols, naphthols, 2,4-pentanediones or acetoacetarilides; wherein
- 10 Y_i is the residue of a bis coupling component selected from the group consisting of anilines, 1,2-dihydroquinolines, 1,2,3,4-tetrahydroquinolines, benzomorpholines (3,4-dihydro- 2H-1,4-benzoxazines), 3-cyano-6-hydroxy-2-pyridones, 2,6-diaminopyridines, 2,3-
- 15 dihydroindoles, naphthylamines, 2-aminothiazoles, or a combination of these; with the provision that two acidic functional groups containing one acidic hydrogen each or a functional group containing two acidic hydrogen are present in the diacidic light absorbing monomer.
- 20 54. The composition of claim 53 wherein Z is selected from the group consisting of:

- 186 -

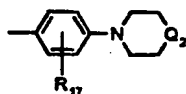
- wherein R_{17} is selected from the group consisting of hydrogen, 1-2 groups selected from C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, $-O$ C_2 - C_6 alkylene-OH, O C_2 - C_6 alkylene- C_1 - C_6 alkanoyloxy, C_1 - C_6 alkylene-OH, C_1 - C_6 alkylene- C_1 - C_6 alkanoyloxy, halogen, carboxy, C_1 - C_6 alkoxycarbonyl, trifluoromethyl, $NHCO_2R_{24}$, $NHCO_2R_{24}$, $NHCON(R_{24})R_{25}$, and $NHSO_2R_{25}$, wherein R_{24} is selected from the group consisting of hydrogen, C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl or aryl, R_{25} is selected from the group consisting of C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl or aryl wherein each C_1 - C_{10} alkyl group in R_{24} and R_{25} may be further substituted with one or more groups selected from the group consisting of C_3 - C_8 cycloalkyl, aryl, aryloxy, arylthio, CO_2H , CO_2 C_1 - C_6 alkyl, cyano, hydroxy, succinimido, C_1 - C_6 alkoxy,



- wherein R_5' is selected from the group consisting of hydrogen, C_1 - C_6 alkyl or aryl; R_{16}' is selected from hydrogen or one or two groups selected from C_1 - C_6 alkyl, halogen and C_1 - C_6 alkoxy; Q is selected from the group consisting of $-O-$, $-N(COR_{10})-$, $-N(R_{10})-$, $-S-$, $-SO_2-$, $-CO_2-$, $-CON(R_{10})$, $-SO_2(R_{10})-$, wherein R_{10} is selected from the group consisting of hydrogen, aryl, C_3 - C_8 cycloalkyl or C_1 - C_{10} alkyl; R_{18} and R_{19} are independently selected from the group consisting of hydrogen, unsubstituted C_1 - C_{10} alkyl, substituted C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl, C_3 - C_8 alkenyl, C_3 - C_8 alkynyl and aryl or R_{18} and R_{19} may be

- 187 -

combined with another element to which they are attached to form a radical Z having the formula

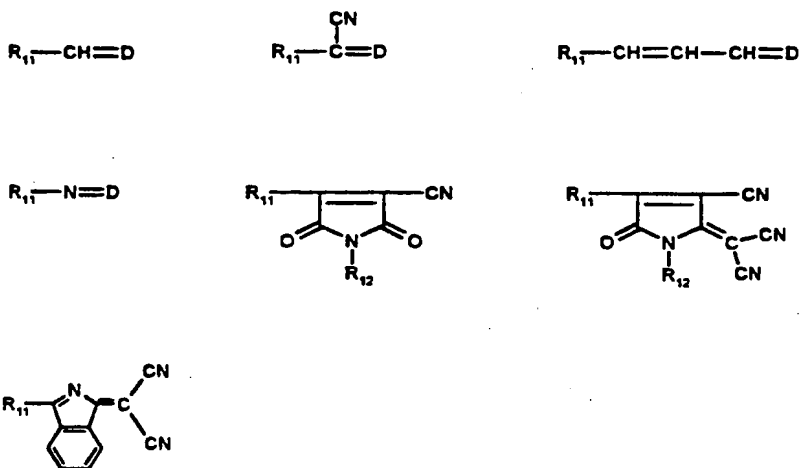


5

wherein Q₂ is selected from the group consisting of a covalent bond, -O-, -S-, -SO₂-, -CO-, -CO₂-, -N-(C₁-C₆ alkyl)-, -N(COC₁-C₆ alkyl)-, -N(SO₂C₁-C₆ alkyl)-, -N(CO aryl)-, or -N(SO₂ aryl); R₂₀, R₂₁ and R₂₂ are independently
 10 selected from the group consisting of hydrogen or C₁-C₆ alkyl; R₂₃ is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₃-C₈ cycloalkyl, heteroaryl or aryl.

55. The composition of claim 26 or 51 wherein the
 15 light absorbing portion of A comprises the residue of at least one light absorbing monomer selected from the group consisting of methine, arylidene, polymethine, azamethine, 3-aryl-2,5-dioxypyrroline, 3-aryl-5-dicyanomethylene-2-oxypyrroline and arylisoindoline and having respectively
 20 the structures:

- 188 -



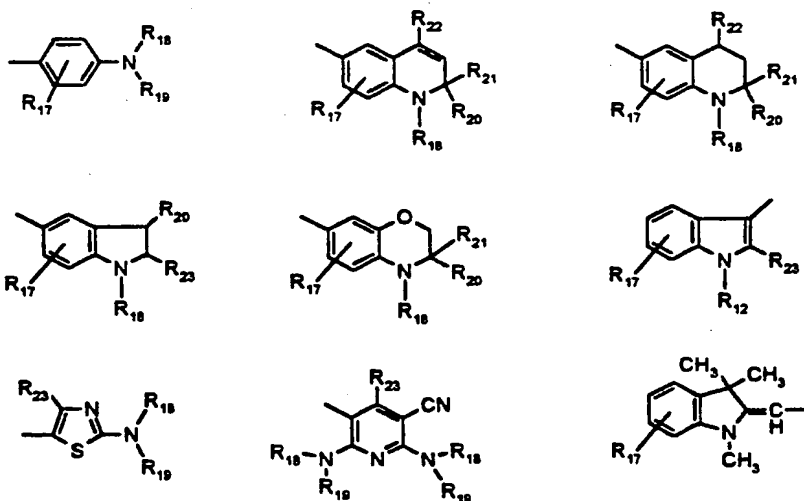
- wherein R₁₁ is the residue of an electron rich aromatic compound selected from the group consisting of an aniline, 1-naphthylamine, 1,2-dihydroquinoline, 1,2,3,4-tetrahydroquinoline, 1,3,3-trimethyl-2-methyleneindole, 1,3-dihydro-2-methylene-1,1,3-trimethyl-2H-benz[e]indole, imidazo [2,1-b] thiazole, benzomorpholine (3,4-dihydro-2H-1,4,benzoxazine), 2,3-dihydroindole, indole, 2-aminothiazole, julolidine (2,3,6,7-tetrahydro-1H, 5H- benz [ij] quinolizine, 1-oxajulolidine, 4H-pyrrolo [3,2,1-ij]-quinoline, phenol, naphthol, thiophenol, pyrrole, pyrazole, furan, thiophene, carbazole, phenothiazine or phenoxazine compound; R₁₂ is selected from the group consisting of hydrogen, C₁-C₁₀ alkyl, C₃-C₈ alkenyl, C₃-C₈-alkynyl, C₃-C₈ cycloalkyl, aryl, (CH₂CH₂O)₁₋₃ R₁₃ and C₁-C₄ alkylene- C₃-C₈ cycloalkylene, wherein the C₁-C₆ alkyl groups may be substituted by at least one group selected from the group consisting of carboxy, C₁-C₆ carbalkoxy, C₁-C₆ alkanoyloxy, cyano, hydroxy, chlorine, fluorine, C₁-C₆ alkoxy, C₃-C₈ cycloalkyl or aryl; R₁₃ is selected from the group consisting of hydrogen, C₁-C₆ alkoxy or C₁-C₆ alkanoyloxy; wherein D is the residue of an active

- 189 -

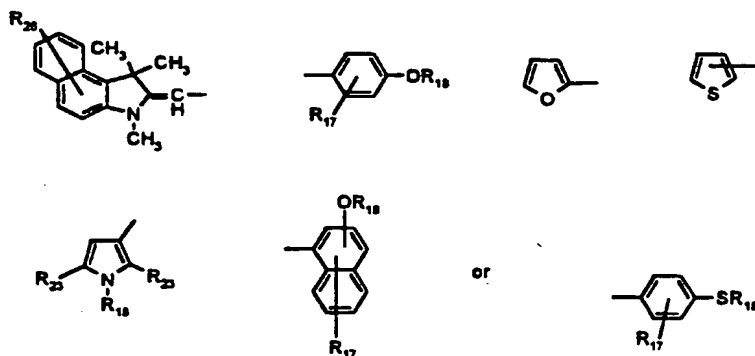
methylene compound selected from the group consisting of
 malononitrile, α -cyanoacetic acid esters, malonic acid
 esters, α -cyanacetic acid amides, α -C₁-C₆
 alkylsulfonylacetonitriles, α -arylsulfonylacetonitriles,
 5 α -C₁-C₆ alkanoylacetonitriles, α -aroylacetonitriles,
 α -heteroarylacetonitriles, bis(heteroaryl)methanes, 1,3-
 indanediones, 2-furanones, benzo-2-furanones, naphtho-2-
 furanones, 2-indolones, 3-cyano-1,6-dihydro-4-methyl-2,6-
 dioxy (2H)-pyridines, benzo (b) thieno-3-ylidene propane
 10 dinitrile-5,5-dioxides, 1,3-bis(dicyanomethylene) indanes,
 barbituric acid, 5-pyrazolones, dimedone, 3-oxo-2,3-
 dihydro-1-benzothiophene-1,1-dioxides or aryl-
 $C(CH_3)C=C(CN)_2$, with the proviso that two acidic functional
 groups containing one acidic hydrogen each, or a
 15 functional group containing two acidic hydrogens are
 present.

56. The composition of claim 55 wherein R₁₁ is
 selected from the group consisting of the electron rich
 aromatic residues corresponding to the structures:

20

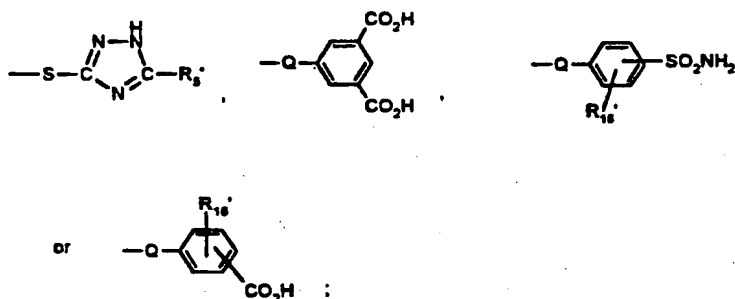


- 190 -

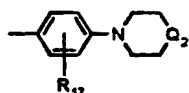


- wherein R₂₆ is selected from the group consisting of hydrogen or a group selected from the group consisting of
- 5 C₁-C₆ alkoxycarbonyl, CO₂H, C₁-C₆ alkyl or C₁-C₆ alkoxy;
- wherein R₁₇ is selected from the group consisting of hydrogen, and 1-2 groups selected from C₁-C₆ alkyl, C₁-C₆ alkoxy, C₁-C₆ alkylthio, -O C₂-C₆ alkylene-OH, O C₂-C₆ alkylene-
- 10 C₁-C₆ alkanoyloxy, C₁-C₆ alkylene-OH, C₁-C₆ alkylene- C₁-C₆ alkanoyloxy, halogen, carboxy, C₁-C₆ alkoxycarbonyl, trifluoromethyl, NHCOR₂₄, NHCO₂R₂₄, NHCON(R₂₄)R₂₅, and NHSO₂R₂₅, wherein R₂₄ is selected from the group consisting of hydrogen, C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl, R₂₅ is selected from the group consisting of C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl wherein each C₁-C₁₀ alkyl
- 15 group in R₂₄ and R₂₅ may be further substituted with one or more groups selected from the group consisting of C₃-C₈ cycloalkyl, aryl, aryloxy, arylthio, CO₂H, CO₂ C₁-C₆ alkyl,

- 191 -



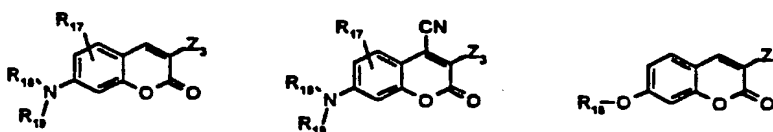
- wherein R_5' is selected from the group consisting of hydrogen, C_1 - C_6 alkyl or aryl; R_{16}' is selected from the group consisting of hydrogen, one or two groups selected from C_1 - C_6 alkyl, halogen and C_1 - C_6 alkoxy; Q is selected from the group consisting of $-O-$, $-N(COR_{10})-$, $-N(R_{10})-$, $-S-$, $-SO_2-$, $-CO_2-$, $CON(R_{10})$, $SO_2(R_{10})-$, wherein R_{10} is selected from the group consisting of hydrogen, aryl, C_3 - C_8 cycloalkyl or C_1 - C_{10} alkyl; R_{18} and R_{19} are independently selected from the group consisting of hydrogen, unsubstituted C_1 - C_{10} alkyl, substituted C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl, C_3 - C_8 alkenyl, C_3 - C_8 alkynyl and aryl or R_{18} and R_{19} may be combined with another element to which they are attached to form a radical Z having the formula



- wherein Q_2 is selected from the group consisting of a covalent bond, $-O-$, $-S-$, $-SO_2-$, $-CO-$, $-CO_2-$, $-N-(C_1-C_6 \text{ alkyl})-$, $-N(CO \text{ } C_1-C_6 \text{ alkyl})-$, $-N(SO_2 \text{ } C_1-C_6 \text{ alkyl})-$, $-N(CO \text{ aryl})-$, or $-N(SO_2 \text{ aryl})-$; R_{20} , R_{21} and R_{22} are independently selected from the group consisting of hydrogen or C_1 - C_6 alkyl; R_{23} is selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_3 - C_8 cycloalkyl, heteroaryl or aryl.

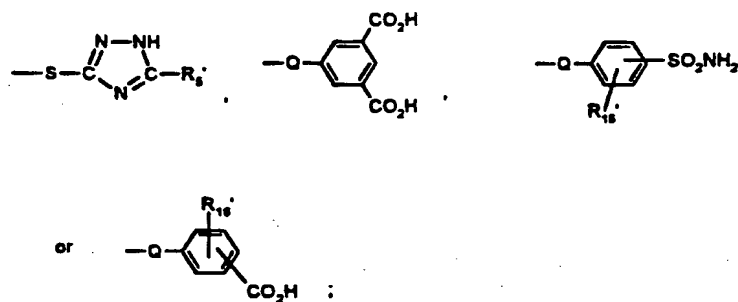
- 192 -

57. The composition of claim 51 wherein the light absorbing portion of A₂ comprises a residue of at least one diacidic coumarin compounds selected from the group consisting of the structures

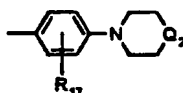


- wherein Z₃ is selected from the group consisting of cyano, C₁-C₆ alkoxycarbonyl, C₁-C₆ alkylsulfonyl, arylsulfonyl, aryl, heteroaryl, formyl, aroyl, C₁-C₆ alkanoyl or -CH=D, wherein R₁₇ is selected from the group consisting of hydrogen, 1-2 groups selected from C₁-C₆ alkyl, C₁-C₆ alkoxy, C₁-C₆ alkylthio, -O C₂-C₆ alkylene-OH, O C₂-C₆ alkylene- C₁-C₆ alkanoyloxy, C₁-C₆ alkylene-OH, C₁-C₆ alkylene- C₁-C₆ alkanoyloxy, halogen, carboxy, C₁-C₆ alkoxycarbonyl, trifluoromethyl, NHCOR₂₄, NHCO₂R₂₄, NHCON(R₂₄)R₂₅, and NHSO₂R₂₅, wherein R₂₄ is selected from the group consisting of hydrogen, C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl, R₂₅ is selected from the group consisting of C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl wherein each C₁-C₁₀ alkyl group in R₂₄ and R₂₅ may be further substituted with one or more groups selected from the group consisting of C₃-C₈ cycloalkyl, aryl, aryloxy, arylthio, CO₂H, CO₂ C₁-C₆ alkyl, cyano, hydroxy, succinimido, C₁-C₆ alkoxy,

- 193 -



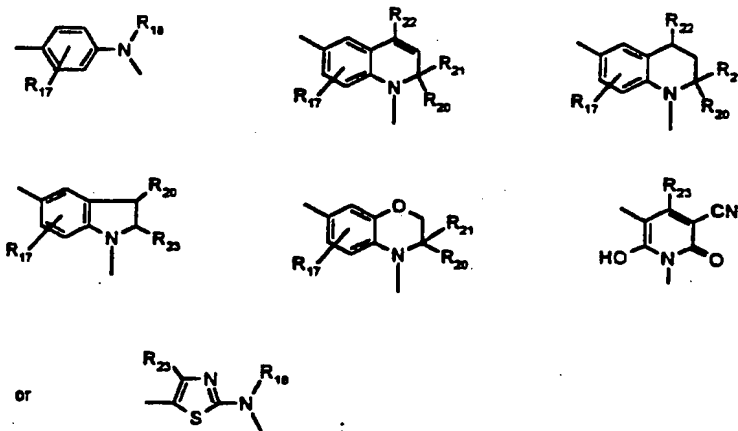
- wherein R_5' is selected from the group consisting of hydrogen, C_1 - C_6 alkyl or aryl; R_{16}' is selected from hydrogen or one or two groups selected from C_1 - C_6 alkyl, halogen, and C_1 - C_6 alkoxy; Q is selected from the group consisting of $-O-$, $-N(COR_{10})-$, $-N(R_{10})-$, $-S-$, $-SO_2-$, $-CO_2-$, $CON(R_{10})$, $SO_2(R_{10})-$, wherein R_{10} is selected from the group consisting of hydrogen, aryl, C_3 - C_8 cycloalkyl or C_1 - C_{10} alkyl; R_{18} and R_{19} are independently selected from the group consisting of hydrogen, unsubstituted C_1 - C_{10} alkyl, substituted C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl, C_3 - C_8 alkenyl, C_3 - C_8 alkynyl and aryl or R_{18} and R_{19} may be combined with another element to which they are attached to form a radical Z having the formula



- wherein Q_2 is selected from the group consisting of a covalent bond, $-O-$, $-S-$, $-SO_2-$, $-CO-$, $-CO_2-$, $-N-(C_1-C_6 \text{ alkyl})-$, $-N(CO \text{ } C_1-C_6 \text{ alkyl})-$, $-N(SO_2 \text{ } C_1-C_6 \text{ alkyl})-$, $-N(CO \text{ aryl})-$, or $-N(SO_2 \text{ aryl})$; R_{20} , R_{21} and R_{22} are independently selected from the group consisting of or C_1 - C_6 alkyl; R_{23} is selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_3 - C_8 cycloalkyl, heteroaryl or aryl; wherein D is the residue of an active methylene compound selected from

the group consisting of malononitrile, α -cyanoacetic acid esters, malonic acid esters, α -cyanacetic acid amides, α -C₁-C₆ alkylsulfonylacetonitriles, α -arylsulfonylacetonitriles, α -C₁-C₆ alkanoylacetonitriles, α -aroylacetonitriles, α -heteroarylacetonitriles, bis(heteroaryl)methanes, 1,3-indanediones, 2-furanones, benzo-2-furanones, naphtho-2-furanones, 2-indolones, 3-cyano-1,6-dihydro-4-methyl-2,6-dioxo (2H)-pyridines, benzo (b) thieno-3-ylidene propane dinitrile-5,5-dioxides, 1,3-bis(dicyanomethylene) indanes, barbituric acid, 5-pyrazolones, dimedone, 3-oxo-2,3-dihydro-1-benzothiophene-1,1-dioxides or aryl-C(CH₃)C=C(CN)₂, with the proviso that two acidic functional groups containing one acidic hydrogen each, or a functional group containing two acidic hydrogens are present.

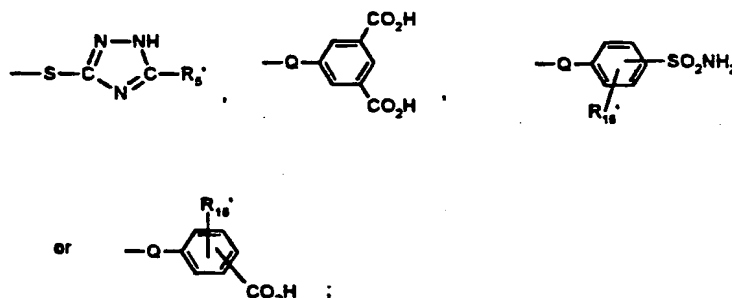
58. The composition of claim 54 wherein the light absorbing portion of A_1 comprises the residue of at least one bis-azo light absorbing monomer wherein the bis coupling component Y_1 is represented by the structure $Z_1-L_1-Z_2$, wherein Z_1 and Z_2 are independently selected from the group consisting of



- 195 -

- wherein, L_1 is bonded to the nitrogen atom of Z_1 and Z_2 ;
 wherein L_1 is selected from the group consisting of C_2 - C_{12}
 alkylene, C_3 - C_8 cycloalkylene, arylene, C_1 - C_4 alkylene-
 5 C_3 - C_8 cycloalkylene- C_1 - C_4 alkylene, C_1 - C_4 alkylene-arylene-
 C_1 - C_4 alkylene, C_2 - C_4 alkylene-O-arylene-O- C_2 - C_4 alkylene,
 $\{C_2$ - C_4 alkylene $O\}_{1-3}$ C_2 - C_4 alkylene, C_2 - C_4 alkylene- S- C_2 - C_4
 alkylene, C_2 - C_4 alkylene-SO₂- C_2 - C_4 alkylene, C_2 - C_4
 alkylene-N(SO₂ C_1 - C_6 alkyl)- C_2 - C_4 alkylene, C_2 - C_4 alkylene-
 10 N(SO₂ aryl)- C_2 - C_4 - alkylene, C_2 - C_4 alkylene- OCO₂- C_2 - C_4
 alkylene, C_2 - C_4 alkylene- O₂C-arylene-CO₂- C_2 - C_4 alkylene,
 C_2 - C_4 alkylene-O₂C- C_1 - C_{12} alkylene-CO₂- C_2 - C_4 alkylene, C_2 - C_4
 alkylene-O₂C- C_3 - C_8 cycloalkylene-CO₂- C_2 - C_4 alkylene, C_2 - C_4
 alkylene-NHCO- C_2 - C_4 alkylene and C_2 - C_4 alkylene-NHSO₂-
 15 C_2 - C_4 alkylene; wherein R_{17} is selected from the group
 consisting of hydrogen, 1-2 groups selected from C_1 - C_6
 alkyl, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, -O C_2 - C_6 alkylene-OH,
 O C_2 - C_6 alkylene- C_1 - C_6 alkanoyloxy, C_1 - C_6 alkylene-OH, C_1 - C_6
 alkylene- C_1 - C_6 alkanoyloxy, halogen, carboxy, C_1 - C_6
 20 alkoxy, carbonyl, trifluoromethyl, NHCOR₂₄, NHCO₂R₂₄,
 NHCON(R₂₄)R₂₅, and NHSO₂R₂₅, wherein R₂₄ is selected from the
 group consisting of hydrogen, C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl
 or aryl, R₂₅ is selected from the group consisting of C_1 - C_{10}
 alkyl, C_3 - C_8 cycloalkyl or aryl wherein each C_1 - C_{10} alkyl
 25 group in R₂₄ and R₂₅ may be further substituted with one or
 more groups selected from the group consisting of C_3 - C_8
 cycloalkyl, aryl, aryloxy, arylthio, CO₂H, CO₂ C_1 - C_6 alkyl,
 cyano, hydroxy, succinimido, C_1 - C_6 alkoxy,

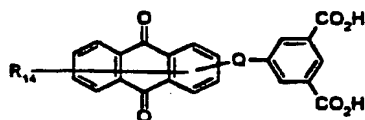
- 196 -



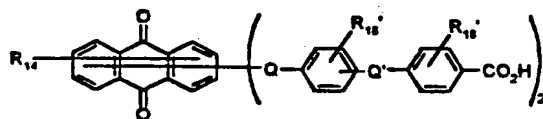
- wherein $\text{R}_{5'}$ is selected from the group consisting of hydrogen, $\text{C}_1\text{—C}_6$ alkyl or aryl; $\text{R}_{16'}$ is selected from
- 5 hydrogen or one or two groups selected from $\text{C}_1\text{—C}_6$ alkyl, halogen and $\text{C}_1\text{—C}_6$ alkoxy; Q is selected from the group consisting of —O— , $\text{—N(COR}_{10}\text{)—}$, $\text{—N(R}_{10}\text{)—}$, —S— , $\text{—SO}_2\text{—}$, $\text{—CO}_2\text{—}$, $\text{CON(R}_{10}\text{)}$, $\text{SO}_2(\text{R}_{10})\text{—}$, wherein R_{10} is selected from the group consisting of hydrogen, aryl, $\text{C}_3\text{—C}_8$ cycloalkyl or $\text{C}_1\text{—C}_{10}$
- 10 alkyl; R_{18} is selected from the group consisting of hydrogen, unsubstituted $\text{C}_1\text{—C}_{10}$ alkyl, substituted $\text{C}_1\text{—C}_{10}$ alkyl, $\text{C}_3\text{—C}_8$ cycloalkyl, $\text{C}_3\text{—C}_8$ alkenyl, $\text{C}_3\text{—C}_8$ alkynyl and aryl; R_{20} , R_{21} , R_{22} are independently selected from the group consisting of or $\text{C}_1\text{—C}_6$ alkyl; R_{23} is selected from the
- 15 group consisting of hydrogen, $\text{C}_1\text{—C}_6$ alkyl, $\text{C}_3\text{—C}_8$ cycloalkyl, heteroaryl or aryl.

59. The diacidic anthraquinone compounds having Formulae

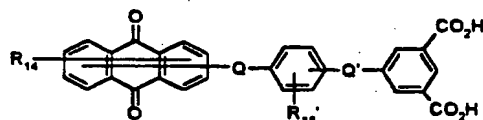
- 197 -



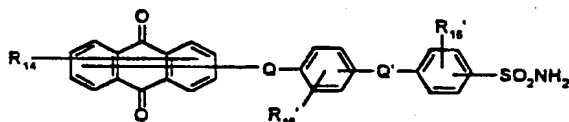
XIV



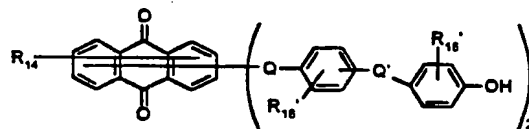
XIXc



XIXd



XIXe

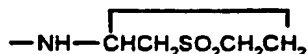


XIXf

- wherein R_{14} is selected from the group consisting of hydrogen, 1-4 groups selected from amino, C_1 - C_{10} alkylamino, C_3 - C_8 alkenylamino, C_3 - C_8 alkynylamino, C_3 - C_8 cycloalkylamino, arylamino, halogen, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, aryl, aroyl, C_1 - C_6 alkanoyl, C_1 - C_6 alkanoyloxy, $NHCO$ C_1 - C_6 alkyl, $NHCO$ aryl, $NHCO_2$ C_1 - C_6 alkyl, $NHSO_2$ C_1 - C_6 alkyl, $NHSO_2$ aryl, C_1 - C_6 alkoxycarbonyl, aryloxy, arylthio, heteroarylthio, cyano, nitro, trifluoromethyl, thiocyno,
- 5 SO_2 C_1 - C_6 alkyl, SO_2 aryl, $-SO_2NH$ C_1 - C_6 alkyl, $-SO_2N(C_1$ - C_6 alkyl) $_2$, $-SO_2N(C_1$ - C_6 alkyl) aryl, $CONH$ C_1 - C_6 alkyl, $CON(C_1$ - C_6 alkyl) $_2$, $CON(C_1$ - C_6 alkyl) aryl, C_1 - C_6 alkyl, furfurylamino,
- 10

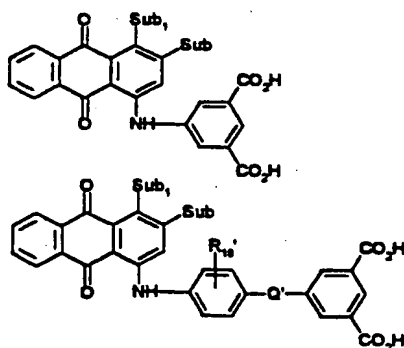
- 198 -

tetrahydrofurfurylamino, 4-(hydroxymethyl)
cyclohexanemethylamino,



- 5 or hydroxy; Q and Q' are independently selected from the group consisting of -O-, -N(COR₁₀)-, -N(SO₂R₁₀)-, -N(R₁₀)-, -S-, -SO₂-, -CO₂-, -CON(R₁₀)-, SO₂N(R₁₀)-, wherein R₁₀ is selected from the group consisting of hydrogen, aryl, C₃-C₈ cycloalkyl, or C₁-C₁₀ alkyl; R₁₆' is selected from hydrogen
10 or one or two groups selected from C₁-C₆ alkyl, halogen and C₁-C₆ alkoxy; wherein each C₁-C₆ alkyl group and C₁-C₆ alkyl group which is a portion of another group may contain at least one substituent selected from the group consisting
15 of hydroxy, cyano, chlorine, fluorine, C₁-C₆ alkoxy, C₃-C₈ cycloalkoxy, C₁-C₆ alkylcyclohexyl, hydroxymethyl cyclohexyl, aryl and heteroaryl; with the provision that two acidic groups containing one acidic proton each or one acidic group containing two acidic hydrogens be present in
20 the compounds of Formula XIV, XIXc, XIXd, XIXe XIXf.

60. The diacidic anthraquinone compounds of claim
57 having the following structures:

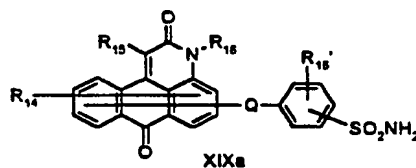
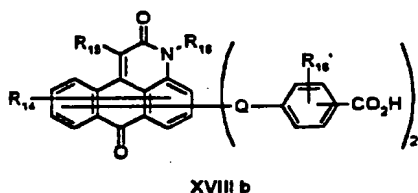
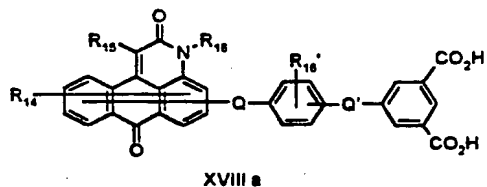
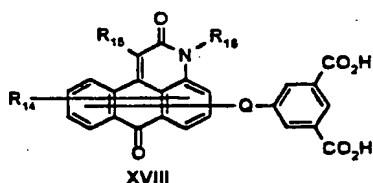


25

- 199 -

- wherein Sub is a substituent selected from the group consisting of halogen, trifluoromethyl, aroyl, C₁-C₆ alkanoyl, C₁-C₆ alkoxycarbonyl, C₁-C₆ alkoxy, C₁-C₆ alkylthio, aryloxy, arylthio, heteroarylthio, cyano, nitro, SO₂NHC₁-C₆ alkyl, SO₂N (C₁-C₆ alkyl)₂, SO₂N (C₁-C₆ alkyl) aryl, CONH C₁-C₆ alkyl, CON (C₁-C₆ alkyl)₂, CON (C₁-C₆ alkyl) aryl, C₁-C₆ alkyl, SO₂ C₁-C₆ alkylsulfonyl and SO₂ aryl; Sub₁ is a substituent selected from the group consisting of amino, C₁-C₁₂ alkylamino, arylamino and C₃-C₈ cycloalkylamino.

61. The diacidic anthrapyridone compounds having Formulae



15

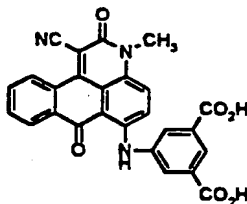
- wherein R₁₄ is selected from the group consisting of hydrogen, 1-4 groups selected from amino, C₁-C₁₀ alkylamino, C₃-C₈ alkenylamino, C₃-C₈ alkynylamino, C₃-C₈ cycloalkylamino, arylamino, halogen, C₁-C₆ alkoxy, C₁-C₆ alkylthio, aryl, aroyl, C₁-C₆ alkanoyl, C₁-C₆ alkanoyloxy, NHCO C₁-C₆ alkyl, NHCOaryl, NHCO₂ C₁-C₆ alkyl, NHSO₂ C₁-C₆ alkyl, NHSO₂ aryl, C₁-C₆ alkoxycarbonyl, aryloxy, arylthio, heteroarylthio, cyano, nitro, trifluoromethyl, thiocyno, SO₂C₁-C₆ alkyl, SO₂ aryl, -SO₂NH C₁-C₆ alkyl, -SO₂N(C₁-C₆

20

- 200 -

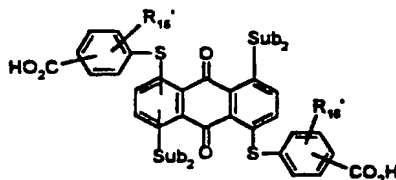
- alkyl)₂, -SO₂N(C₁-C₆ alkyl) aryl, CONH C₁-C₆ alkyl, CON(C₁-C₆ alkyl)₂, CON(C₁-C₆ alkyl) aryl, C₁-C₆ alkyl or hydroxy; Q and Q' are independently selected from the group consisting of -O-, -N(COR₁₀)-, -N(SO₂R₁₀)-, -N(R₁₀)-, -S-,
- 5 -SO₂-, -CO₂-, -CON(R₁₀)-, SO₂N (R₁₀)-, wherein R₁₀ is selected from the group consisting of hydrogen, aryl, C₃-C₈ cycloalkyl, or C₁-C₁₀ alkyl; R₁₁ is selected from the group consisting of hydrogen, cyano, C₁-C₆ alkylamino, C₁-C₆ alkoxy, halogen, arylthio, aryl, heteroaryl,
- 10 heteroarylthio, C₁-C₆ alkoxycarbonyl, aroyl or arylsulfonyl; R₁₂ is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₃-C₈ cycloalkyl and aryl; R₁₃' is selected from the group consisting of hydrogen or one or two groups selected from C₁-C₆ alkyl, halogen and C₁-C₆
- 15 alkoxy; wherein each C₁-C₆ alkyl group and C₁-C₆ alkyl group which is a portion of another group may contain at least one substituent selected from the group consisting of hydroxy, cyano, chlorine, fluorine, C₁-C₆ alkoxy, C₃-C₈ cycloalkoxy, C₁-C₆ alkylcyclohexyl, hydroxymethyl
- 20 cyclohexyl, aryl and heteroaryl; with the provision that two acidic groups containing one acidic proton each or one acidic group containing two acidic hydrogens be present in the compounds of Formula XVIII, XVIIIa, XVIIIb, and XIXa.

- 25 62. The diacidic anthrapyridone compound of claim 61 having the structure:

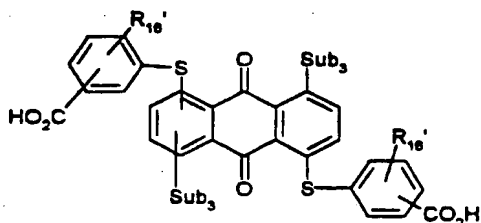


- 30 63. The diacidic anthraquinone compounds having the formulae

- 201 -

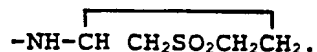


or



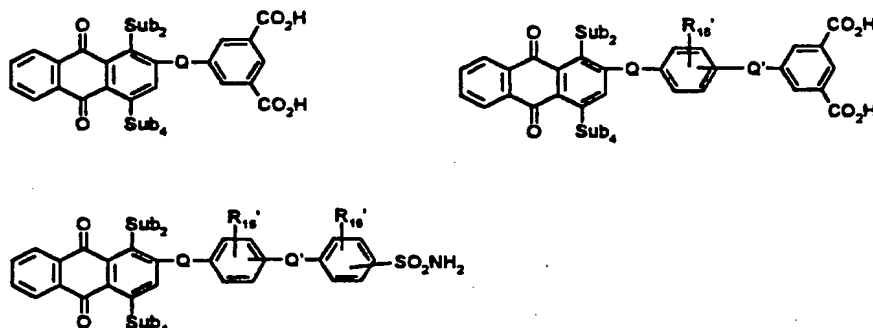
5

where R_{16}' is selected from the group consisting of hydrogen or one or two groups selected from C_1 - C_6 alkyl, halogen and C_1 - C_6 alkoxy; and Sub_3 is a substituent selected from C_1 - C_6 alkylthio, arylthio and heteroarylthio and Sub_2 is a substituent selected from the group consisting of amino, C_1 - C_{10} alkylamino, C_3 - C_8 alkenylamino, C_3 - C_8 alkynylamino, C_3 - C_8 cycloalkylamino, arylamino, furfurylamino, tetrahydrofurfurylamino, 4-(hydroxymethyl) cyclohexanemethylamino, $NHCO$ C_1 - C_6 alkyl, $NHCO$ aryl, $NHCO_2$ C_1 - C_6 alkyl, $NHSO_2$ C_1 - C_6 alkyl, $NHSO_2$ aryl and



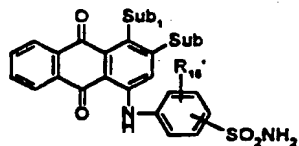
20 64. The diacidic anthraquinone compounds of claim 59 having the formulae:

- 202 -



- wherein Sub₂ is as defined in claim 63; Sub₄ is selected from the group consisting of Sub₂, NHCO C₁-C₆ alkyl, NHCO C₁-C₆ alkyl, NHCO aryl, NHSO₂ C₁-C₆ alkyl, NHSO₂ aryl, C₁-C₆ alkylthio, arylthio, heteroarylthio and hydroxy; Q is selected from the group consisting of -O-, S-, -SO₂-; Q' is selected from the group consisting of -O-, -N(COR₁₀)-, -N(SO₂R₁₀)-, -N(R₁₀)-, -S-, -SO₂-, -CO₂-, -CON(R₁₀)-, SO₂N(R₁₀)-, wherein R₁₀ is selected from the group consisting of hydrogen, aryl, C₃-C₈ cycloalkyl, or C₁-C₁₀ alkyl.

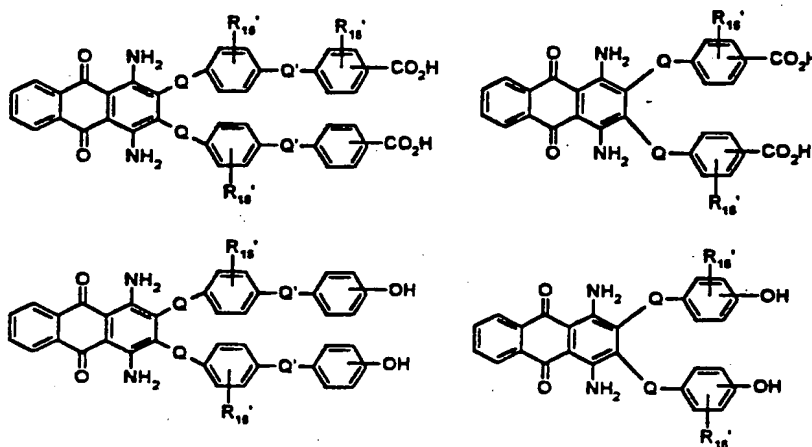
65. The diacidic anthraquinone compounds having the formula



wherein Sub, Sub₁ and R₁₆' are as defined in claim 60.

66. The diacidic anthraquinone compounds having the structures

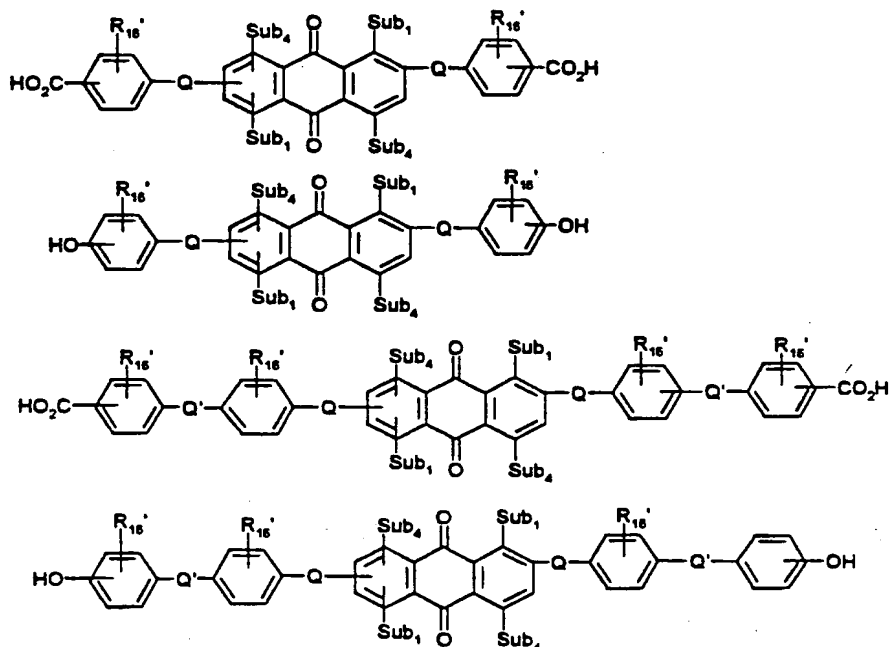
- 203 -



wherein Q is selected from the group consisting of -O-, -S- and -SO₂-; Q' is selected from the group consisting of -O-, -N(COR₁₀)-, -N(SO₂R₁₀)-, -N(R₁₀)-, -S-, -SO₂-, -CO₂-, -CON(R₁₀)-, SO₂N(R₁₀)-, wherein R₁₀ is selected from the group consisting of hydrogen, aryl, C₃-C₈ cycloalkyl, or C₁-C₁₀ alkyl; and R₁₆' is selected from the group consisting of hydrogen or one or two groups selected from C₁-C₆ alkyl, halogen and C₁-C₆ alkoxy.

67. The diacidic anthraquinone compounds having the structures:

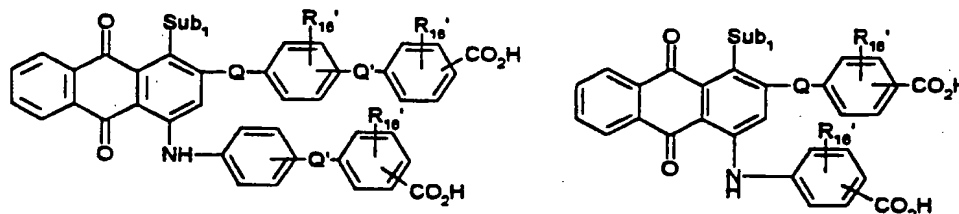
- 204 -



- wherein Sub₁ defined as in claim 60, Sub₄ is defined as in claim 64, Q is selected from the group consisting of -O-, -S- and -SO₂-; Q' is selected from the group consisting of -O-, -N(COR₁₀)-, -N(SO₂R₁₀)-, -N(R₁₀)-, -S-, -SO₂-, -CO₂-, -CON(R₁₀)-, SO₂N(R₁₀)-, wherein R₁₀ is selected from the group consisting of hydrogen, aryl, C₃-C₈ cycloalkyl, or C₁-C₁₀ alkyl; and R₁₆' is selected from the group consisting of hydrogen or one or two groups selected from C₁-C₆ alkyl, halogen and C₁-C₆ alkoxy.

68. The diacidic anthraquinone compounds having the structures:

- 205 -



wherein Q is selected from the group consisting of -O-, -S- and -SO₂-; Sub₁ is a substituent selected from the group consisting of amino, C₁-C₁₂ alkylamino, arylamino and C₃-C₈ cycloalkylamino; Q' is selected from the group consisting of -O-, -N(COR₁₀)-, -N(SO₂R₁₀)-, -N(R₁₀)-, -S-, -SO₂-, -CO₂-, -CON(R₁₀)-, SO₂N (R₁₀)-, wherein R₁₀ is selected from the group consisting of hydrogen, aryl, C₃-C₈ cycloalkyl, or C₁-C₁₀ alkyl; and R₁₆' is selected from the group consisting of hydrogen or one or two groups selected from C₁-C₆ alkyl, halogen and C₁-C₆ alkoxy.

69. The diacidic azo and disazo compounds of the formulae R₆-N=N-Z (VI) and R₆-N=N-R₇-N=N-Z (VII), respectively wherein R₆ is the residue of a diazotized aromatic or heteroaromatic amine and Z is the residue of an electron rich coupling component selected from the group consisting of the classes of anilines, 1-aminonaphthalenes, 1,2-dihydroquinolines, 1,2,3,4-tetrahydroquinolines, benzomorpholines (3,4-dihydro-2H-1,4-benzoxazine), pyrazolones, pyrazoles, 3-cyano-6-hydroxy-2-pyridones, 2,3-dihydroindoles, indoles, 4-hydroxycoumarins, 4-hydroxy-2-quinolones, imidazo[2,1-b]thiazoles, julolidines (2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizines), 1-oxajulolidines, 1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolines, 2,6-diamino-3-cyanopyridines, 2-aminothiazoles, 2-aminothiophenes, 5,5-dimethyl-1,3-cyclohexanedione (dimedone), phenols, naphthols, 2,4-pentanediones or acetoacetarilides; R₇ is a divalent aromatic or heteroaromatic radical selected from the group consisting of the classes of 1,4-phenylene, naphthalene -1, 4-diyl, thiazol-2,5-diyl and thiophene -

- 206 -

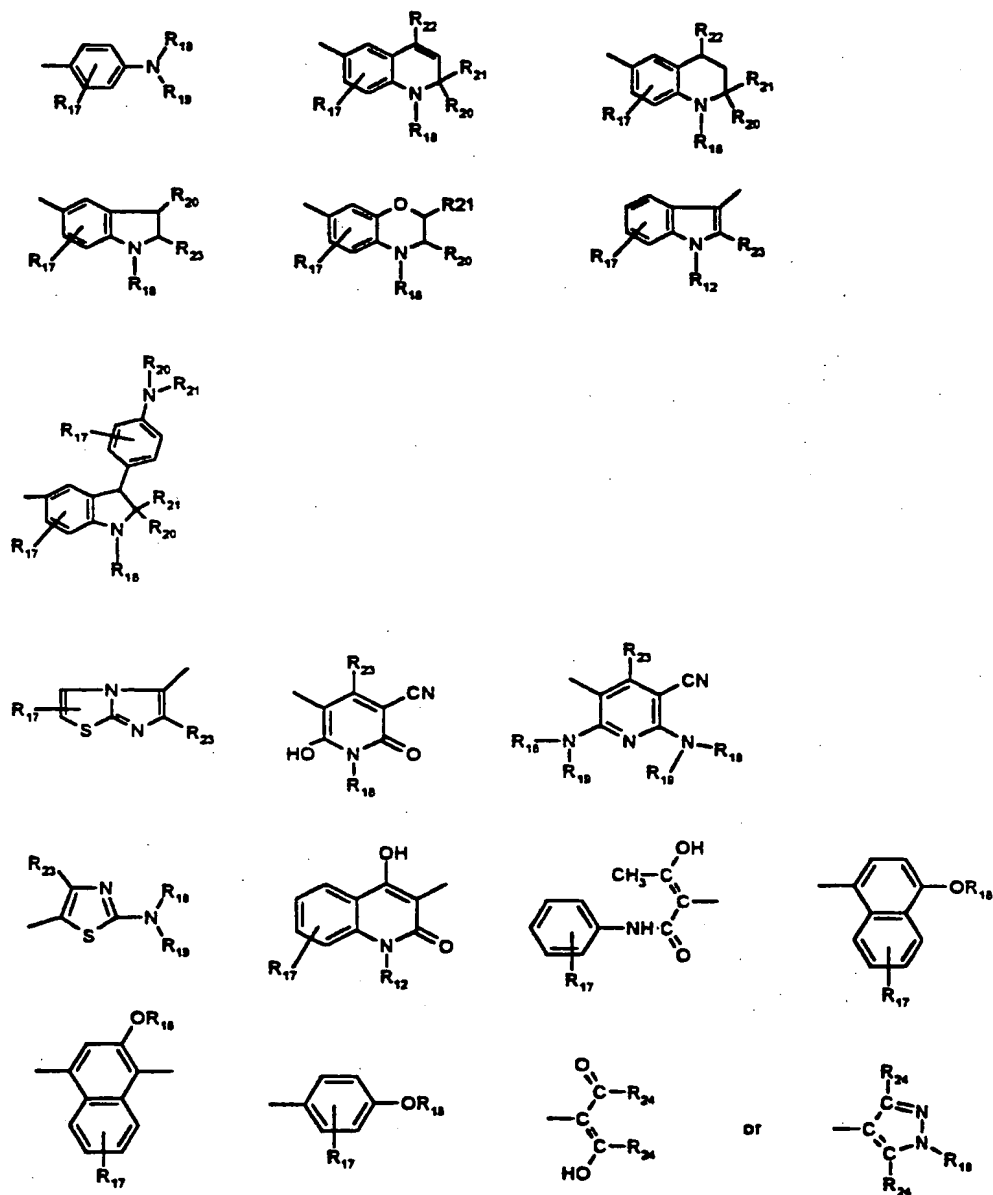
2,5-diyl; with the provision that R₆ or Z contains a carboxy (-CO₂H) acidic group and that another acidic group selected from the group consisting of (-CO₂H) , -SH, -OH attached to aromatic ring, -CONHCO-, -SO₂NH-CO-, -SO₂NH-SO₂-, and 1(H) 1, 2, 4-triazol-3-yl, be present on or as part of R₆ or Z so that each R₆ and Z moiety contains one acidic group.

70. The diacidic azo and disazo compounds of claim 69 wherein R₆ and Z each contain a carboxy (-CO₂H) acidic group.

71. The diacidic azo and bisazo compounds of claim 69 wherein R₆ is the residue of substituted diazotized aromatic or heteroaromatic amine compounds derived from the classes of aniline, 1-aminonaphthalene, 1-aminoanthraquinone, 4-aminoazobenzene, 2-aminothiazole, 2-aminobenzothiazole, 3-amino- 2,1-benzisothiazole, 2-aminothieno[2,3-d]thiazole, 5-aminoisothiazole, 5-aminopyrazole, 4-aminopyrazoloisothiazole, 2-amino-1,3,4-thiadiazole, 5-amino-1,2,4-thiadiazole, 5-amino-1,2,3-triazole, 2-amino-1,3,4-triazole, 2(5) aminoimidazole, 3-aminopyridine, 2(3) aminothiophene, 2(3) aminobenzo[b]thiophene, 2-aminothieno[3,2-b]thiophene, 3-aminothieno[2,3-c]isothiazole, 3-amino-7-benz-2,1-isothiazole, 3-aminobenzothienoisothiazole, 3-aminoisothiazole[3,4-d]pyrimidine, 5-amino-1,2,3-triazole, 3(4) aminophthalimide and 5(6) amino-1,2-benzisothiazolon-1,1-dioxide and Z is the residue of an electron rich coupling coupler residue selected from the group consisting of the following:

30

- 207 -

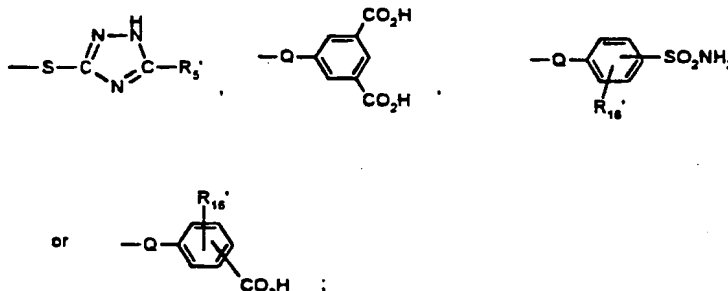


5

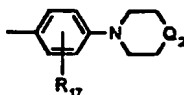
wherein R₁₇ is selected from the group consisting of hydrogen, 1-2 groups selected from C₁-C₆ alkyl, C₁-C₆

- 208 -

- alkoxy, C₁-C₆ alkylthio, -O C₂-C₆ alkylene-OH, O C₂-C₆ alkylene- C₁-C₆ alkanoyloxy, C₁-C₆ alkylene-OH, C₁-C₆ alkylene- C₁-C₆ alkanoyloxy, halogen, carboxy, C₁-C₆ alkoxycarbonyl, trifluoromethyl, NHCOR₂₄, NHCO₂R₂₄,
 5 NHCON(R₂₄)R₂₅, and NHSO₂R₂₅, wherein R₂₄ is selected from the group consisting of hydrogen, C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl, R₂₅ is selected from the group consisting of C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl wherein each C₁-C₁₀ alkyl group in R₂₄ and R₂₅ may be further substituted with one or
 10 more groups selected from the group consisting of C₃-C₈ cycloalkyl, aryl, aryloxy, arylthio, CO₂H, CO₂ C₁-C₆ alkyl, cyano, hydroxy, succinimido, C₁-C₆ alkoxy,



- 15 wherein R₅', R₁₆' and Q are as defined in claim 63; R₁₈ and R₁₉ are independently selected from the group consisting of hydrogen, unsubstituted C₁-C₁₀ alkyl, substituted C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl, C₃-C₈ alkenyl, C₃-C₈ alkynyl and
 20 aryl or R₁₈ and R₁₉ may be combined with another element to which they are attached to form a radical Z having the formula



25

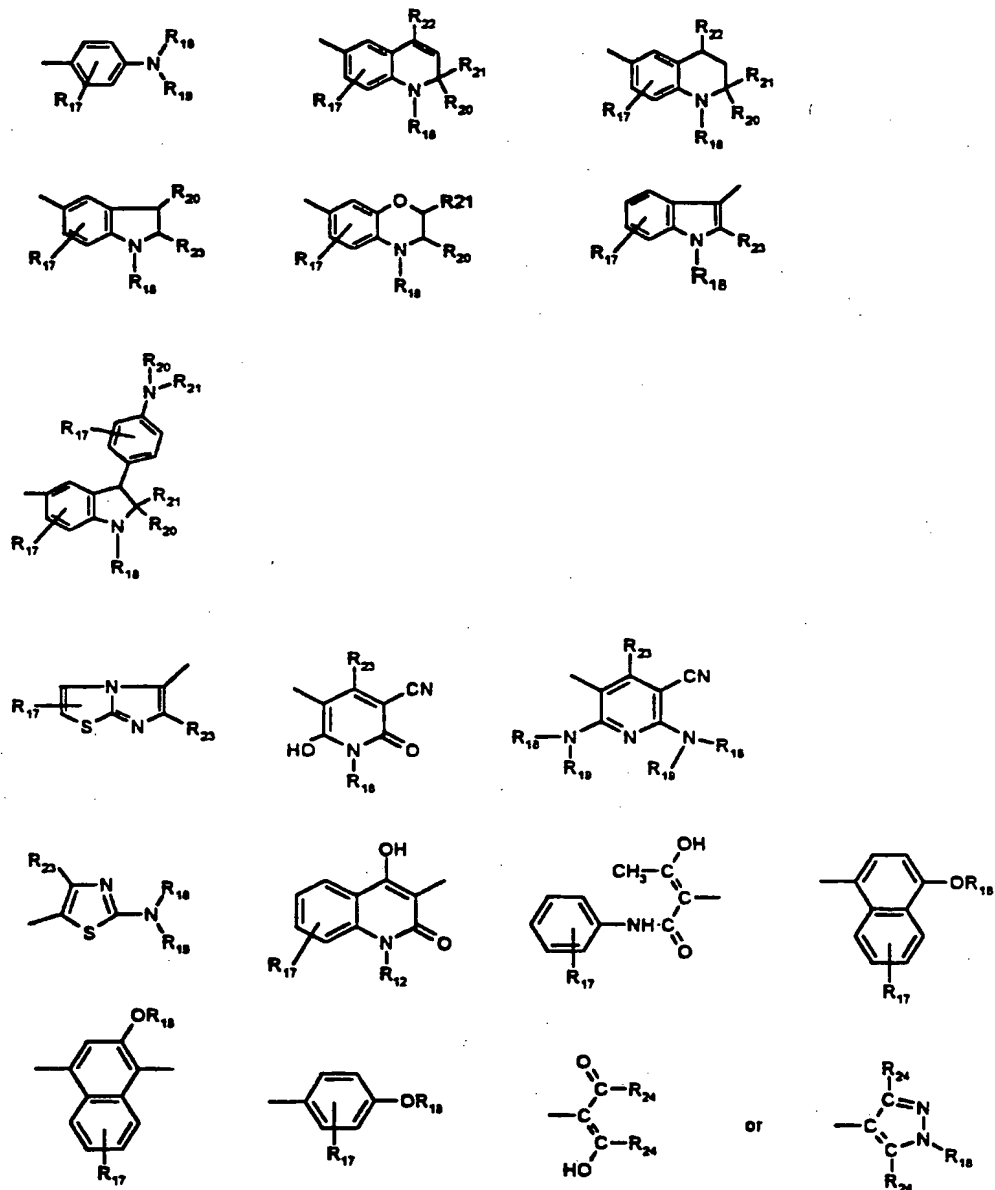
- 209 -

wherein Q₂ is selected from the group consisting of a covalent bond, -O-, -S-, -SO₂-, -CO-, -CO₂-, -N-(C₁-C₆ alkyl)-, -N(CO C₁-C₆ alkyl)-, -N(SO₂ C₁-C₆ alkyl)-, -N(CO aryl)-, or -N(SO₂ aryl); R₂₀, R₂₁ and R₂₂ are independently
5 selected from the group consisting of or C₁-C₆ alkyl; R₂₃ is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₃-C₈ cycloalkyl, heteroaryl or aryl.

72. The diacidic azo and disazo compounds of claim 69 of the formulae R₆-N=N-Z (VI) and R₆-N=N-R₇-N=N-Z (VII),
10 respectively, wherein one of R₆ and Z contains two carboxy (-CO₂H) acidic groups.

73. The diacidic azo and disazo compounds of claim 69 or 72 wherein R₆ is the residue of a diazotized substituted or unsubstituted diazotized aromatic or
15 heteromatic amine compound derived from an amine selected from aniline, 1-aminonaphthalene, 1-aminoanthraquinone, 4-aminoazobenzene, 2-aminothiazole, 2-aminobenzothiazole, 3-amino-2,1-benzisothiazole, 2-aminothieno[2,3-d]thiazole, 5-aminoisothiazole, 5-aminopyrazole,
20 4-aminopyrazoloisothiazole, 2-amino-1,3,4-thiadiazole, 5-amino-1,2,4-thiadiazole, 5-amino-1,2,3-triazole, 2-amino-1,3,4-triazole, 2(5) aminoimidazole, 3-aminopyridine, 2(3) aminothiophene, 2(3) aminobenzo[b]thiophene, 2-aminothieno[3,2-b]thiophene, 3-aminothieno[2,3-
25 c]isothiazole, 3-amino-7-benz-2,1-isothiazole, 3-aminobenzothienoisothiazole, 3-aminoisothiazole[3,4-d]pyrimidine, 5-amino-1,2,3-triazole, 3(4) aminophthalimide and 5(6) amino-1,2-benzisothiazolon-1,1-dioxide and Z is the residue of an electron rich coupling
30 component selected from the group consisting of the following:

- 210 -

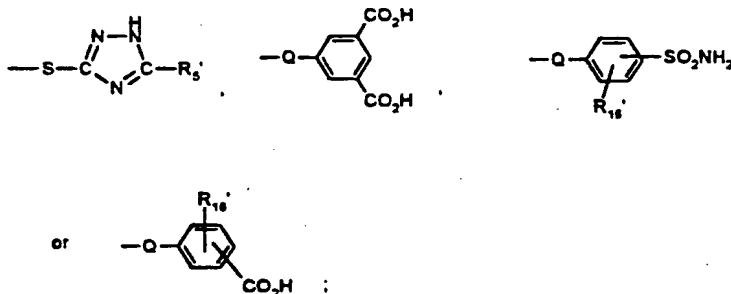


5

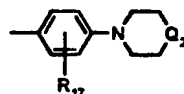
wherein R₁₇ is selected from the group consisting of hydrogen, 1-2 groups selected from C₁-C₆ alkyl, C₁-C₆

- 211 -

- alkoxy, C₁-C₆ alkylthio, -O C₂-C₆ alkylene-OH, O C₂-C₆ alkylene- C₁-C₆ alkanoyloxy, C₁-C₆ alkylene-OH, C₁-C₆ alkylene- C₁-C₆ alkanoyloxy, halogen, carboxy, C₁-C₆ alkoxy, carbonyl, trifluoromethyl, NHCOR₂₄, NHCO₂R₂₄,
 5 NHCON(R₂₄)R₂₅, and NHSO₂R₂₅, wherein R₂₄ is selected from the group consisting of hydrogen, C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl, R₂₅ is selected from the group consisting of C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl wherein each C₁-C₁₀ alkyl group in R₂₄ and R₂₅ may be further substituted with one or
 10 more groups selected from the group consisting of C₃-C₈ cycloalkyl, aryl, aryloxy, arylthio, CO₂H, CO₂ C₁-C₆ alkyl, cyano, hydroxy, succinimido, C₁-C₆ alkoxy,



- 15 wherein R₅', R₁₆' and Q are as defined in claim 63; R₁₈ and R₁₉ are independently selected from the group consisting of hydrogen, unsubstituted C₁-C₁₀ alkyl, substituted C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl, C₃-C₈ alkenyl, C₃-C₈ alkynyl and
 20 aryl or R₁₈ and R₁₉ may be combined with another element to which they are attached to form a radical Z having the formula

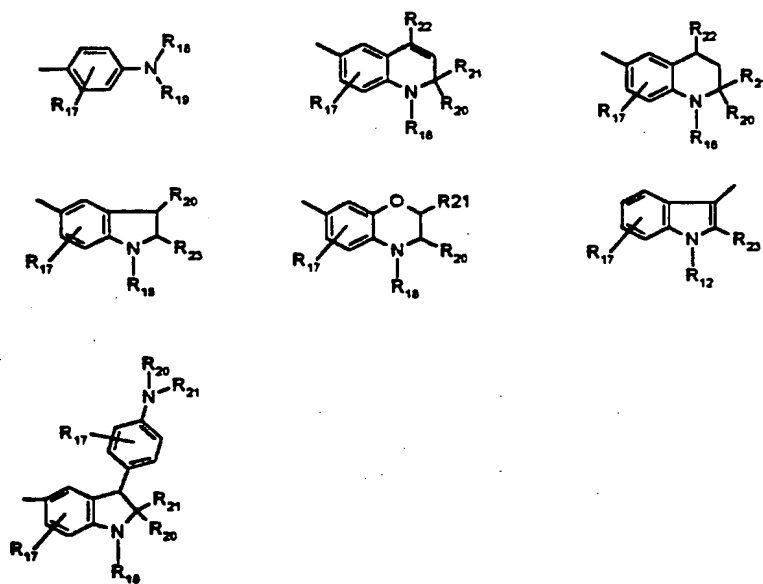


25

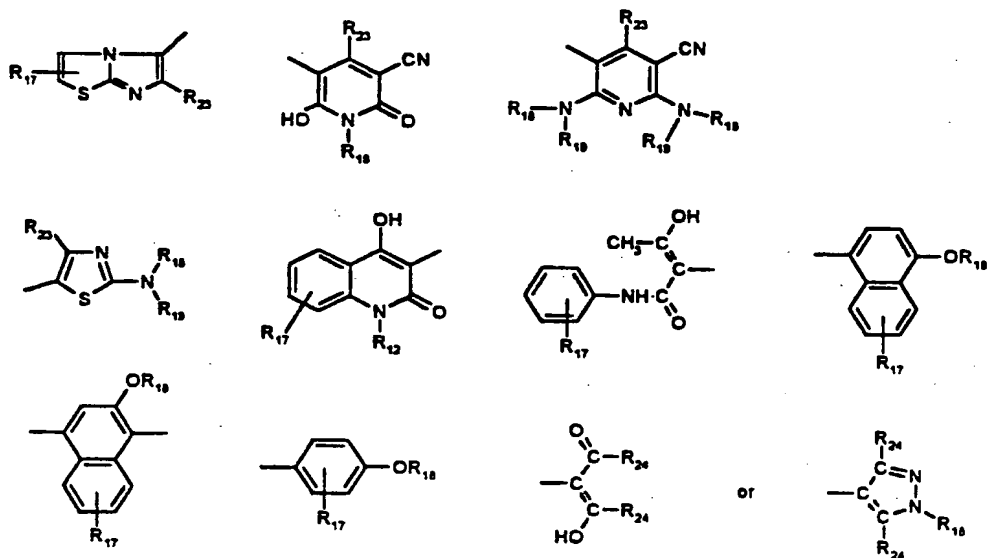
- 212 -

wherein Q₂ is selected from the group consisting of a covalent bond, -O-, -S-, -SO₂-, -CO-, -CO₂-, -N-(C₁-C₆ alkyl)-, -N(CO C₁-C₆ alkyl)-, -N(SO₂ C₁-C₆ alkyl)-, -N(CO aryl)-, or -N(SO₂ aryl); R₂₀, R₂₁ and R₂₂ are independently
 5 selected from the group consisting of or C₁-C₆ alkyl; R₂₃ is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₃-C₈ cycloalkyl, heteroaryl or aryl.

74. The diacidic azo and bisazo compounds of claim 72 wherein Z is an electron rich coupler selected from the
 10 group consisting of the following:

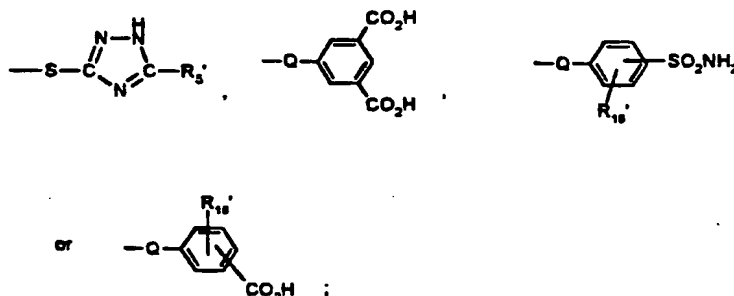


- 213 -

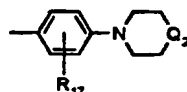


- wherein R₁₇ is selected from the group consisting of
- 5 hydrogen, 1-2 groups selected from C₁-C₆ alkyl, C₁-C₆ alkoxy, C₁-C₆ alkylthio, -O C₂-C₆ alkylene-OH, O C₂-C₆ alkylene- C₁-C₆ alkanoyloxy, C₁-C₆ alkylene-OH, C₁-C₆ alkylene- C₁-C₆ alkanoyloxy, halogen, carboxy, C₁-C₆ alkoxycarbonyl, trifluoromethyl, NHCOR₂₄, NHCO₂R₂₄,
 - 10 NHCON(R₂₄)R₂₅, and NHSO₂R₂₅, wherein R₂₄ is selected from the group consisting of hydrogen, C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl, R₂₅ is selected from the group consisting of C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl or aryl wherein each C₁-C₁₀ alkyl group in R₂₄ and R₂₅ may be further substituted with one or
 - 15 more groups selected from the group consisting of C₃-C₈ cycloalkyl, aryl, aryloxy, arylthio, CO₂H, CO₂ C₁-C₆ alkyl, cyano, hydroxy, succinimido, C₁-C₆ alkoxy,

- 214 -



wherein $R_{5'}$, $R_{18'}$ and Q are as defined in claim 63; R_{18} and R_{19} are independently selected from the group consisting of hydrogen, unsubstituted C_1 - C_{10} alkyl, substituted C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl, C_3 - C_8 alkenyl, C_3 - C_8 alkynyl and aryl or R_{18} and R_{19} may be combined with another element to which they are attached to form a radical Z having the formula



wherein Q_2 is selected from the group consisting of a covalent bond, $-O-$, $-S-$, $-SO_2-$, $-CO-$, $-CO_2-$, $-N-(C_1-C_6$ alkyl)-, $-N(CO C_1-C_6$ alkyl)-, $-N(SO_2 C_1-C_6$ alkyl)-, $-N(CO$ aryl)-, or $-N(SO_2$ aryl); R_{20} , R_{21} and R_{22} are independently selected from the group consisting of or C_1 - C_6 alkyl; R_{23} is selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_3 - C_8 cycloalkyl, heteroaryl or aryl.

75. The diacidic bisazo compounds having the formula $R_6-N=N-Y_1-N=N-R_6$ (VIIa) wherein R_6 is the residue of a substituted diazotized aromatic or heteroaromatic amine compound derived from the classes of aniline, 1-aminonaphthalene, 1-aminoanthraquinone, 4-aminoazobenzene, 2-aminothiazole, 2-aminobenzothiazole, 3-amino-2,1-benzisothiazole, 2-aminothieno[2,3-d]thiazole,

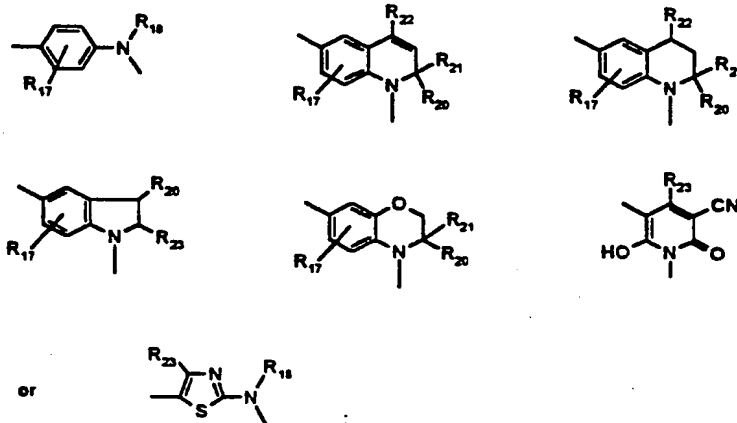
- 215 -

- 5-aminoisothiazole, 5-aminopyrazole,
4-aminopyrazoloisothiazole, 2-amino-1,3,4-thiadiazole, 5-
amino-1,2,4-thiadiazole, 5-amino-1,2,3-triazole, 2-amino-
1,3,4-triazole, 2(5) aminoimidazole, 3-aminopyridine, 2(3)
5 aminothiophene, 2(3) aminobenzo[b]thiophene, 2-
aminothieno[3,2-b]thiophene, 3-aminothieno[2,3-
c]isothiazole, 3-amino-7-benz- 2,1-isothiazole, 3-
aminobenzothienoisothiazole, 3-aminoisothiazole[3,4-
d]pyrimidine, 5-amino- 1,2,3-triazole, 3(4)
10 aminophthalimide and 5(6) amino-1,2-benzisothiazolon-1,1-
dioxide and Y₁ is the residue of a bis coupling component
selected from the group consisting of the classes of
anilines, 1,2-dihydroquinolines, 1,2,3,4-
tetrahydroquinolines, benzomorpholines (3,4-dihydro-
15 2H-1,4-benzoxazines), 3-cyano-6-hydroxy-2-pyridones, 2,6-
diaminopyridines, 2,3-dihydroindoles, naphthylamines, 2-
aminothiazoles, or a combination of these, with the
provision that each R₆ group contain one acidic group
selected from the group consisting of -CO₂H, -SH, -OH
20 attached to an aromatic ring, -NHCONH-, -SO₂NHCO-, -
SO₂NHSO₂-, 1 (H)-1,2,4-triazol-3-yl-, imidazolyl,
benzimidazolyl, pyrazolyl and -SO₂H attached to aromatic
ring.

76. The bis-azo compounds of claim 75 wherein each
25 R₆ group contains one carboxy (-CO₂H) group.

77. The bis-azo compounds of claim 75 wherein Y₁ has
the formula Z₁-L₁-Z₂ wherein Z₁ and Z₂ are independently
selected from the group consisting of:

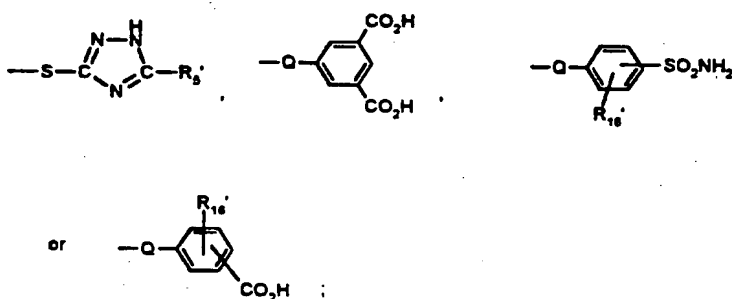
- 216 -



- wherein L_1 is bonded to the nitrogen atom of Z_1 and Z_2 ;
 wherein L_1 is selected from the group consisting of C_2 - C_{12}
 5 alkylene, C_3 - C_8 cycloalkylene, arylene, C_1 - C_4 alkylene-
 C_3 - C_8 cycloalkylene- C_1 - C_4 alkylene, C_1 - C_4 alkylene-arylene-
 C_1 - C_4 alkylene, C_2 - C_4 alkylene-O-arylene-O- C_2 - C_4 alkylene,
 (C_2 - C_4 alkylene O_{1-3} C_2 - C_4 alkylene, C_2 - C_4 alkylene- S- C_2 - C_4
 alkylene, C_2 - C_4 alkylene- SO_2 - C_2 - C_4 alkylene, C_2 - C_4
 10 alkylene-N(SO_2 C_1 - C_6 alkyl)- C_2 - C_4 alkylene, C_2 - C_4 alkylene-
 N(SO_2 aryl)- C_2 - C_4 - alkylene, C_2 - C_4 alkylene- OCO_2 - C_2 - C_4
 alkylene, C_2 - C_4 alkylene- O_2C -arylene- CO_2 - C_2 - C_4 alkylene,
 C_2 - C_4 alkylene- O_2C - C_1 - C_{12} alkylene- CO_2 - C_2 - C_4 alkylene, C_2 - C_4
 alkylene- O_2C - C_3 - C_8 cycloalkylene- CO_2 - C_2 - C_4 alkylene, C_2 - C_4
 15 alkylene-NHCO- C_2 - C_4 alkylene and C_2 - C_4 alkylene-NH SO_2 -
 C_2 - C_4 alkylene; R_{17} is selected from the group consisting
 of hydrogen, 1-2 groups selected from C_1 - C_6 alkyl, C_1 - C_6
 alkoxy, C_1 - C_6 alkylthio, -O C_2 - C_6 alkylene-OH, O C_2 - C_6
 alkylene- C_1 - C_6 alkanoyloxy, C_1 - C_6 alkylene-OH, C_1 - C_6
 20 alkylene- C_1 - C_6 alkanoyloxy, halogen, carboxy, C_1 - C_6
 alkoxycarbonyl, trifluoromethyl, $NHCO_2R_{24}$, $NHCO_2R_{24}$,
 $NHCON(R_{24})R_{25}$, and $NHSO_2R_{25}$, wherein R_{24} is selected from the
 group consisting of hydrogen, C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl
 or aryl, R_{25} is selected from the group consisting of C_1 - C_{10}

- 217 -

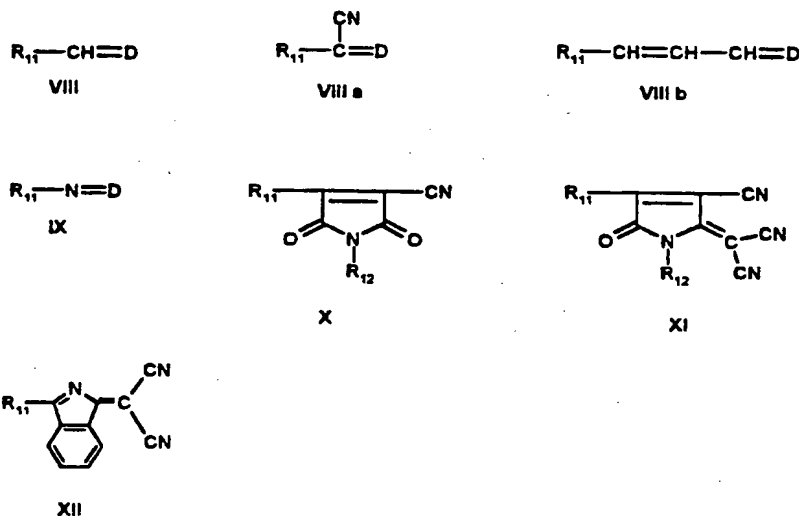
- alkyl, C₃-C₈ cycloalkyl or aryl wherein each C₁-C₁₀ alkyl group in R₂₄ and R₂₅ may be further substituted with one or more groups selected from the group consisting of C₃-C₈ cycloalkyl, aryl, aryloxy, arylthio, CO₂H, CO₂ C₁-C₆ alkyl, cyano, hydroxy, succinimido, C₁-C₆ alkoxy,



- wherein R₅', R₁₆' and Q are as defined in claim 63; R₁₆ is selected from the group consisting of hydrogen, a group selected from the group consisting of unsubstituted C₁-C₁₀ alkyl, substituted C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl, C₃-C₈ alkenyl, C₃-C₈ alkynyl and aryl; R₂₀, R₂₁ and R₂₂ are independently selected from the group consisting of or C₁-C₆ alkyl; R₂₃ is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₃-C₈ cycloalkyl, heteroaryl or aryl.

78. The diacidic methine, arylidene, polymethine, azamethine, 3-aryl-2,5-dioxypyrroline, 3-aryl-5-dicyanomethylene -2-oxypyrroline and aryl isoindoline corresponding to formulae VIII, VIIIa, VIIIb, IX, X, XI and XII, respectively:

- 218 -

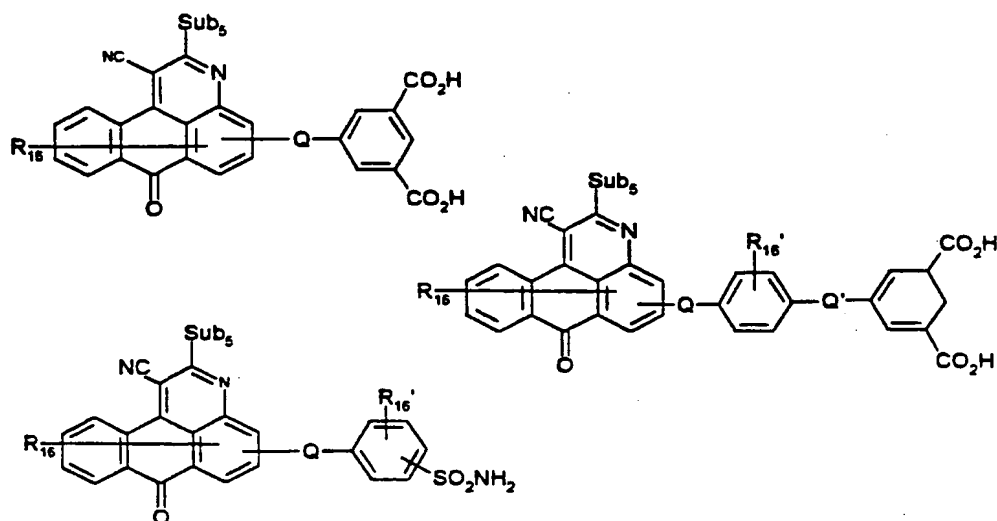


wherein R_{11} is the residue of an aniline, 1-naphthylamine, 1,2-dihydroquinoline, 1,2,3,4-tetrahydroquinoline, 1,3,3-trimethyl-2-methyleneindole, 1,3-dihydro-2-methylene-1,1,3-trimethyl-2H-benz[e]indole, imidazo [2,1-b]thiazole, benzomorpholine (3,4-dihydro-2H-1,4-benzoxazine), indole, 2,3-dihydroindole, 2-aminothiazole, julolidine (2,3,6,7-tetrahydro-1H, 5H-benz [ij] quinolizine, 1-oxajulolidine, 4H-pyrrolo [3,2,1-ij]-quinoline, phenol, naphthol, thiophenol, pyrrole, pyrazole, furan, thiophene, carbazole, phenothiazine or phenoxazine compound; R_{12} is selected from the group consisting of hydrogen, C_1-C_{10} alkyl, C_3-C_8 alkenyl, C_3-C_8 -alkynyl, C_3-C_8 cycloalkyl, aryl, $(CH_2CH_2O)_{1-3}$ R_{13} and C_1-C_4 alkylene- C_3-C_8 cycloalkylene, wherein the C_1-C_6 alkyl groups may be substituted by at least one group selected from the group consisting of carboxy, C_1-C_6 carbalkoxy, C_1-C_6 alkanoyloxy, cyano, hydroxy, chlorine, fluorine, C_1-C_6 alkoxy, C_3-C_8 cycloalkyl or aryl; R_{13} is selected from the group consisting of hydrogen, C_1-C_6 alkoxy or C_1-C_6 alkanoyloxy; wherein D is the residue of an active

- 219 -

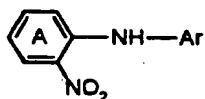
- methylene compound selected from the group consisting of malononitrile, α -cyanoacetic acid esters, malonic acid esters, α -cyanacetic acid amides, α -C₁-C₆ alkylsulfonylacetonitriles, α -arylsulfonylacetonitriles, α -C₁-C₆ alkanoylacetonitriles, α -aroylacetonitriles, α -heteroarylacetonitriles, bis(heteroaryl)methanes, 1,3-indanediones, 2-furanones, benzo-2-furanones, naphtho-2-furanones, 2-indolones, 3-cyano-1,6-dihydro-4-methyl-2,6-dioxy (2H)-pyridines, benzo (b) thieno-3-ylidene propane dinitrile-5,5-dioxides, 1,3-bis (dicyanomethylene) indanes, barbituric acid, 5-pyrazolones, dimedone, 3-oxo-2,3-dihydro-1-benzothiophene-1,1-dioxides or aryl-C(CH₃)C=C(CN)₂, with the proviso that two acidic functional groups selected from the group consisting of -CO₂H, -SH, -OH attached to aromatic ring, -CONHCO-, -SO₂NHCO-, -SO₂NHSO₂-, 1(H) -1,2,4,-triazol-3-yl, imidazolyl, benzimidazolyl, pyrazolyl and SO₂H attached to aromatic ring be present or one diacidic sulfamoyl (-SO₂NH₂) be present.
79. The diacidic anthrapyridine compounds having the structures:

- 220 -



wherein Sub₅ is a substituent selected from the group
 5 consisting of -N (C₁-C₁₀ alkyl)₂, -N (C₁-C₁₀ alkyl) aryl, -
 N (C₁-C₁₀ alkyl) C₃-C₈ cycloalkyl, morpholino and
 piperidino; Q and Q' are selected from the group
 consisting of -NH-, -O-, -S- and -SO₂-, R₁₆' is selected
 10 from the group consisting of hydrogen, C₁-C₆ alkyl, halogen
 and C₁-C₆ alkoxy.

80. The nitroarylamine compounds having the
 structure:



15 wherein ring A may be substituted with one or more groups
 selected from the group consisting of halogen, -SO₂N(C₁-C₆
 alkyl)₂, -CON (C₁-C₆ alkyl)₂, SO₂ C₁-C₆ alkyl, SO₂ aryl, C₁-
 C₆ alkyl, C₁-C₆ alkoxy, carboxy, and nitro; Ar is
 phthalimid-3 (or 4)-yl, phenyl, or 2-thienyl, or these
 20 substituted with one or more groups selected from the

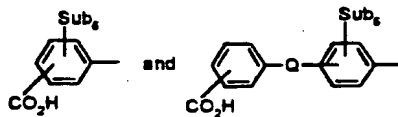
- 221 -

group consisting of halogen, C₁-C₆ alkyl, C₁-C₆ alkoxy, 1(H)-1,2,4,-triazolyl-3-ylthio, carboxy, or hydroxy, with the provision that two acidic groups be present.

81. The nitroarylamine compounds of claim 80
 5 wherein two carboxy groups are present on Ar or ring A or one carboxy is present on each of Ar and ring A.

82. The diacidic compounds of claim 72, having the formula R₆-N=N-Z, wherein R₆ is selected from the group consisting of

10



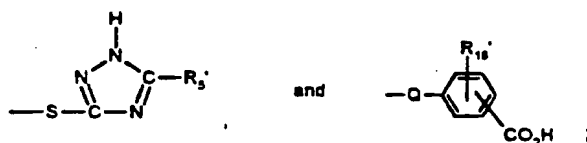
- wherein Sub₆ is selected from the group consisting of hydrogen, one to four groups selected from C₁-C₁₀ alkyl,
 15 C₁-C₆ alkoxy, C₃-C₈ cycloalkyl, halogen, , C₁-C₆ alkoxy carbonyl, formyl, C₁-C₆ alkanoyl, C₁-C₆ alkanoyloxy, dicyanovinyl, C₃-C₈-cycloalkanoyl, thiocyno, trifluoroacetyl, cyano, carbamoyl, -CONH C₁-C₆ alkyl, CONHaryl, CON(C₁-C₆ alkyl)₂, SO₂N(C₁-C₆ alkyl)₂, CONH C₃-C₈
 20 cycloalkyl, aryl, aroyl, -N(C₁-C₆ alkyl)SO₂ C₁-C₆ alkyl, NHCO C₁-C₆ alkyl, NHCO C₃-C₈ cycloalkyl, NHCOaryl, NHCO₂ C₁-C₆ alkyl, NHCONH C₁-C₆ alkyl, NHCONHaryl, N(C₁-C₆ alkyl)aryl, arylazo, heteroaryl, aryloxy, arylthio, C₃-C₈ cycloalkoxy, heteroarylazo, heteroarylthio, arylsulfonyl,
 25 tricyanovinyl, aryloxysulfonyl, C₁-C₆ alkylsulfonyl, trifluoromethyl, fluorosulfonyl, trifluoromethylsulfonyl, thiocyno, nitro and CH=D, wherein D is the residue of an active methylene compound selected from the group consisting of malononitrile, α-cyanoacetic acid esters,
 30 malonic acid esters, α-cyanoacetic acid amides, α-C₁-C₆ alkylsulfonylacetonitriles, α-arylsulfonylacetonitriles, α-C₁-C₆ alkanoylacetonitriles, α-aroylacetonitriles, α-heteroarylacetonitriles, bis(heteroaryl)methanes, 1,3-

- 222 -

indanediones, 2-furanones, benzo-2-furanones, naphtho-2-furanones, 2-indolones, 3-cyano-1,6-dihydro-4-methyl-2,6-dioxy (2H)-pyridines, benzo (b) thieno-3-ylidene propane dinitrile-5,5-dioxides, 1,3-bis (dicyanomethylene)

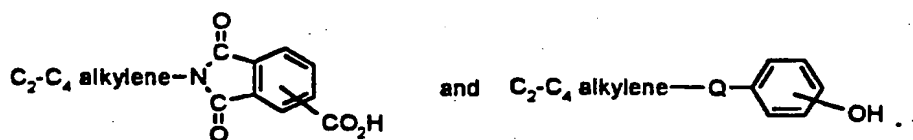
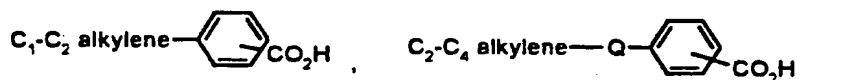
- 5 indanes, barbituric acid, 5-pyrazolones, dimedone, 3-oxo-2,3-dihydro-1-benzothiophene-1,1-dioxides and aryl- $C(CH_3)C=C(CN)_2$; with the provision that one acidic group selected from the group consisting of carboxy,

10



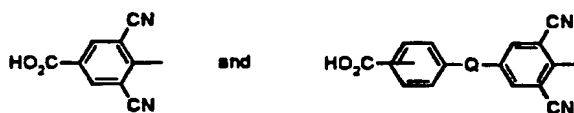
be present on either R₁₇, R₁₈, R₁₉ or R₂₄; Q is selected from the group consisting of -O-, -S-, and -SO₂-.

83. The compounds of claim 82 wherein R₁₈ is
15 selected from the group consisting of C₁-C₁₀ alkylene-CO₂H,

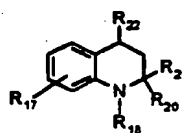
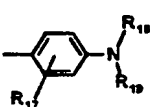


84. The diacidic compounds of claim 82 wherein R₆ is
20 selected from the group consisting of

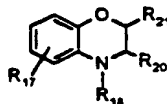
- 223 -



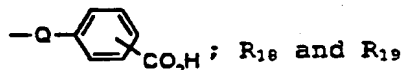
and Z is selected from



and

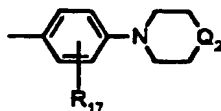


wherein R_{17} is selected from the group consisting of hydrogen, 1-2 groups selected from C_1 - C_6 alkyl, C_1 - C_6 alkoxy, halogen, $NHCO_2R_{24}$, $NHCO_2R_{24}$ and $NHCONHR_{24}$, wherein R_{24} is selected from the group consisting of hydrogen, C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl and aryl; wherein each C_1 - C_{10} alkyl group in R_{24} may be further substituted with one or more groups selected from the group consisting of C_3 - C_8 cycloalkyl, carboxy, aryl, aryloxy, arylthio, CO_2 C_1 - C_6 alkyl, cyano, hydroxy, succinimido, C_1 - C_6 alkoxy and



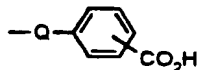
are independently selected from the group consisting of hydrogen, unsubstituted C_1 - C_{10} alkyl, substituted C_1 - C_{10} alkyl, C_3 - C_8 alkyl, C_3 - C_8 alkenyl and aryl or R_{18} and R_{19} may be combined with another element to which they are attached to from a radical

- 224 -



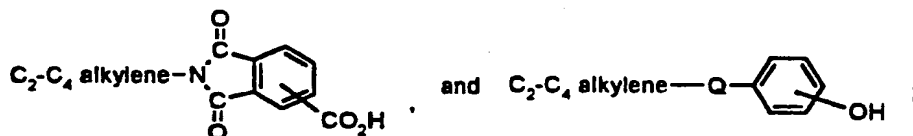
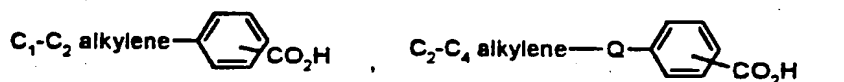
wherein Q_2 is selected from the group consisting of -O-, -S-, -SO₂-, -CO-, -CO₂-, -N (COC₁-C₆ alkyl)-, -N (SO₂ C₁-C₆ alkyl)-, -N (COaryl)-, and -N (SO₂ aryl)-; R_{20} , R_{21} , and R_{22} are independently selected from the group consisting of or C₁-C₆ alkyl; with the provision that either R_{17} contain one acidic group selected from the group consisting of carboxy and

10



with the groups R_{18} and R_{19} being void of acidic groups or R_{17} may be void of acidic groups and R_{18} be selected from the group consisting of C₁-C₁₀ alkylene -CO₂H,

15



wherein Q is selected from the group consisting of -O-, -S-, and -SO₂-; with the final provision that only two carboxy groups be present.

20

85 The diacidic compounds of claim 61 having the formula $R_6-N=N-Z$, wherein R_6 is the residue of a

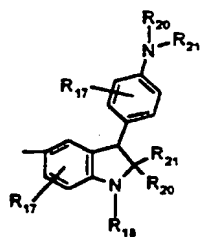
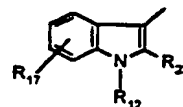
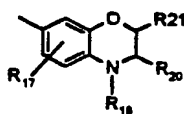
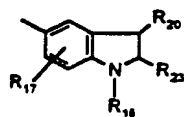
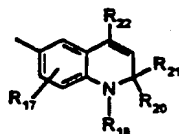
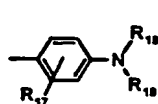
[illegible]

5

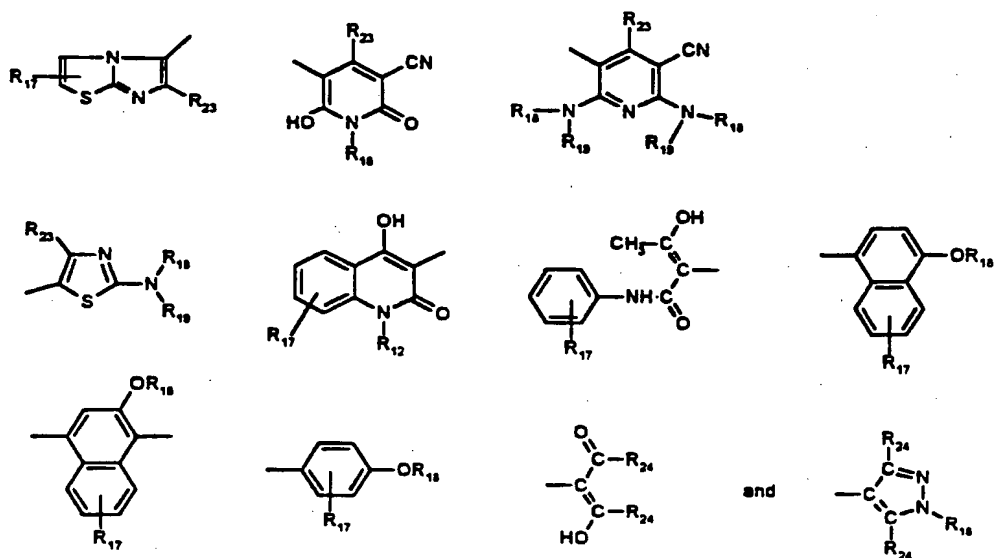
wherein Sub₇ is one or more substituent selected from the group consisting of hydrogen, halogen, C₁-C₆ alkyl, aryl, heteroaryl, C₁-C₆ alkanoyl, CONH C₁-C₆ alkyl, SO₂ C₁-C₆ alkyl, SO₂ aryl, C₁-C₆ alkoxycarbonyl, aroyl, cyano, formyl and nitro; Sub₈ is selected from the group consisting of hydrogen, halogen, C₁-C₆ alkyl, aryl and heteroaryl; Sub₉ is selected from the group consisting of C₁-C₆ alkyl C₃-C₈ cycloalkyl, C₃-C₈ alkenyl, and aryl; Sub₁₀ is selected from the group consisting of cyano, nitro, C₁-C₆ alkylsulfonyl, arylthio, arylsulfonyl and C₁-C₆ alkoxycarbonyl; Sub₁₁ is hydrogen one or more substituents selected from the group consisting of C₁-C₆ alkyl, cyano, nitro, halogen, arylthio,

- 226 -

heteroarylthio, arylsulfonyl, aryloxy and C_1 - C_6 alkylsulfonyl; Q is selected from the group consisting of -O-, -S- and -SO₂-; wherein Z is a coupling component selected from the group consisting of



- 227 -

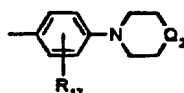


- 5 wherein R_{17} is selected from the group consisting of hydrogen, 1-2 groups selected from C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, $-O$ C_2 - C_6 alkylene-OH, O C_2 - C_6 alkylene- C_1 - C_6 alkanoyloxy, C_1 - C_6 alkylene-OH, C_1 - C_6 alkylene- C_1 - C_6 alkanoyloxy, halogen, C_1 - C_6 alkoxycarbonyl, trifluoromethyl, $NHCO_2R_{24}$, $NHCO_2R_{24}$, and $NHCONHR_{24}$, wherein
- 10 R_{24} is selected from the group consisting of hydrogen, C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl and aryl; wherein each C_1 - C_{10} alkyl group in R_{24} may be further substituted with one or more groups selected from the group consisting of C_3 - C_8
- 15 cycloalkyl, aryl, aryloxy, arylthio, CO_2 C_1 - C_6 alkyl, cyano, hydroxy, succinimido, C_1 - C_6 alkoxy,

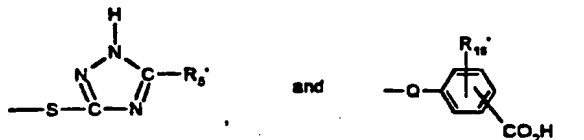


- 228 -

wherein R_5' is selected from the group consisting of hydrogen, C_1-C_6 alkyl and aryl; R_{16}' is selected from the group consisting of hydrogen, one or two groups selected from C_1-C_6 alkyl, halogen and C_1-C_6 alkoxy; R_{18} and R_{19} are independently selected from the group consisting of hydrogen, unsubstituted C_1-C_{10} alkyl, substituted C_1-C_{10} alkyl, C_3-C_8 cycloalkyl, C_3-C_8 alkenyl, C_3-C_8 alkynyl and aryl or R_{18} and R_{19} may be combined with another element to which they are attached to form a radical Z having the formula



wherein Q_2 is selected from the group consisting of a covalent bond, -O-, -S-, -SO₂-, -CO-, -CO₂-, -N-(C_1-C_6 alkyl)-, -N(CO C_1-C_6 alkyl)-, -N(SO₂ C_1-C_6 alkyl)-, -N(CO aryl)-, or -N(SO₂ aryl); R_{20} , R_{21} and R_{22} are independently selected from the group consisting of or C_1-C_6 alkyl; R_{23} is selected from the group consisting of hydrogen, C_1-C_6 alkyl, C_3-C_8 cycloalkyl, heteroaryl or aryl; with the provision that one acidic group selected from the group consisting of carboxy,

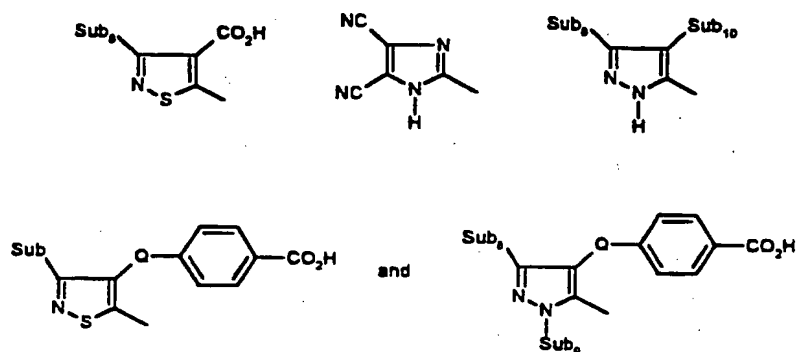


25

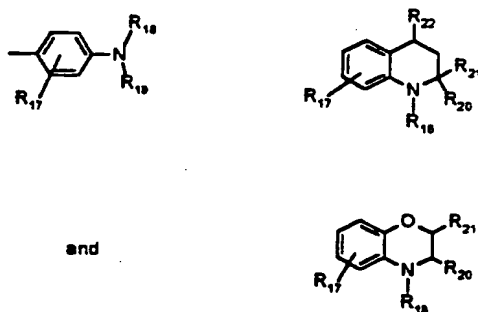
be present on either R_{17} , R_{18} , R_{19} or R_{24} ; Q is selected from the group consisting of -O-, -S-, and -SO₂-; with the provision that R_6 and Z each contain one acidic group.

- 229 -

86. The diacidic compounds of claim 85 having the formula $R_6-N=N-Z$, wherein R_6 is selected from the group consisting of

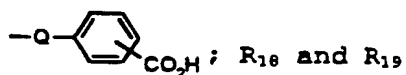


and Z is selected from the group consisting of

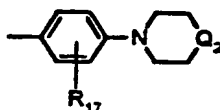


wherein R_{17} is selected from the group consisting of hydrogen, 1-2 groups selected from C_1 - C_6 alkyl, C_1 - C_6 alkoxy, halogen, $NHCOR_{24}$, $NHCO_2R_{24}$ and $NHCONHR_{24}$, wherein R_{24} is selected from the group consisting of hydrogen, C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl and aryl; wherein each C_1 - C_{10} alkyl group in R_{24} may be further substituted with one or more groups selected from the group consisting of C_3 - C_8 cycloalkyl, carboxy, aryl, aryloxy, arylthio, CO_2 C_1 - C_6 alkyl, cyano, hydroxy, succinimido, C_1 - C_6 alkoxy and

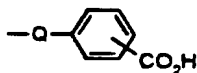
- 230 -



are independently selected from the group consisting of hydrogen, unsubstituted C₁-C₁₀ alkyl, substituted C₁-C₁₀ alkyl, C₃-C₈ alkyl, C₃-C₈ alkenyl and aryl or R₁₈ and R₁₉ may be combined with another
 5 element to which they are attached to from a radical

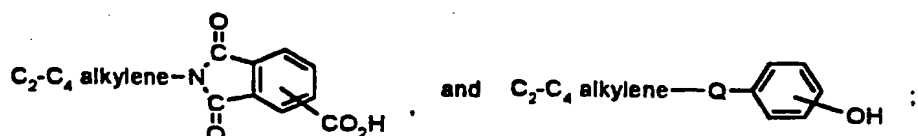
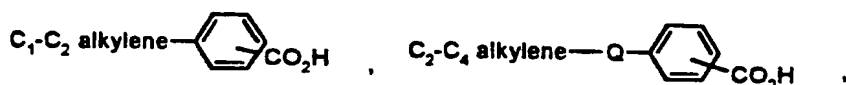


wherein Q₂ is selected from the group consisting of -O-, -S-, -SO₂, -CO-, -CO₂, -N (COC₁-C₆ alkyl)-, -N (SO₂ C₁-C₆ alkyl)-, -N (COaryl)-, and -N (SO₂ aryl)-; R₂₀, R₂₁, and R₂₂ are independently selected from the group consisting of or C₁-C₆ alkyl; with the provision that either R₁₇ contain one
 10 acidic group selected from the group consisting of carboxy
 15 and



with the groups R₁₈ and R₁₉ being void of acidic groups or
 20 R₁₇ may be void of acidic groups and R₁₈ be selected from the group consisting of C₁-C₁₀ alkylene -CO₂H,

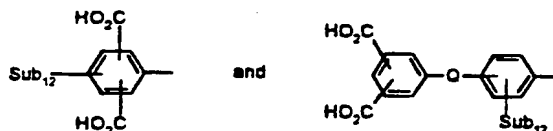
- 231 -



wherein Q is selected from the group consisting of - O -,
- S -, and - SO₂ -; with the final provision that only two
5 carboxy groups be present.

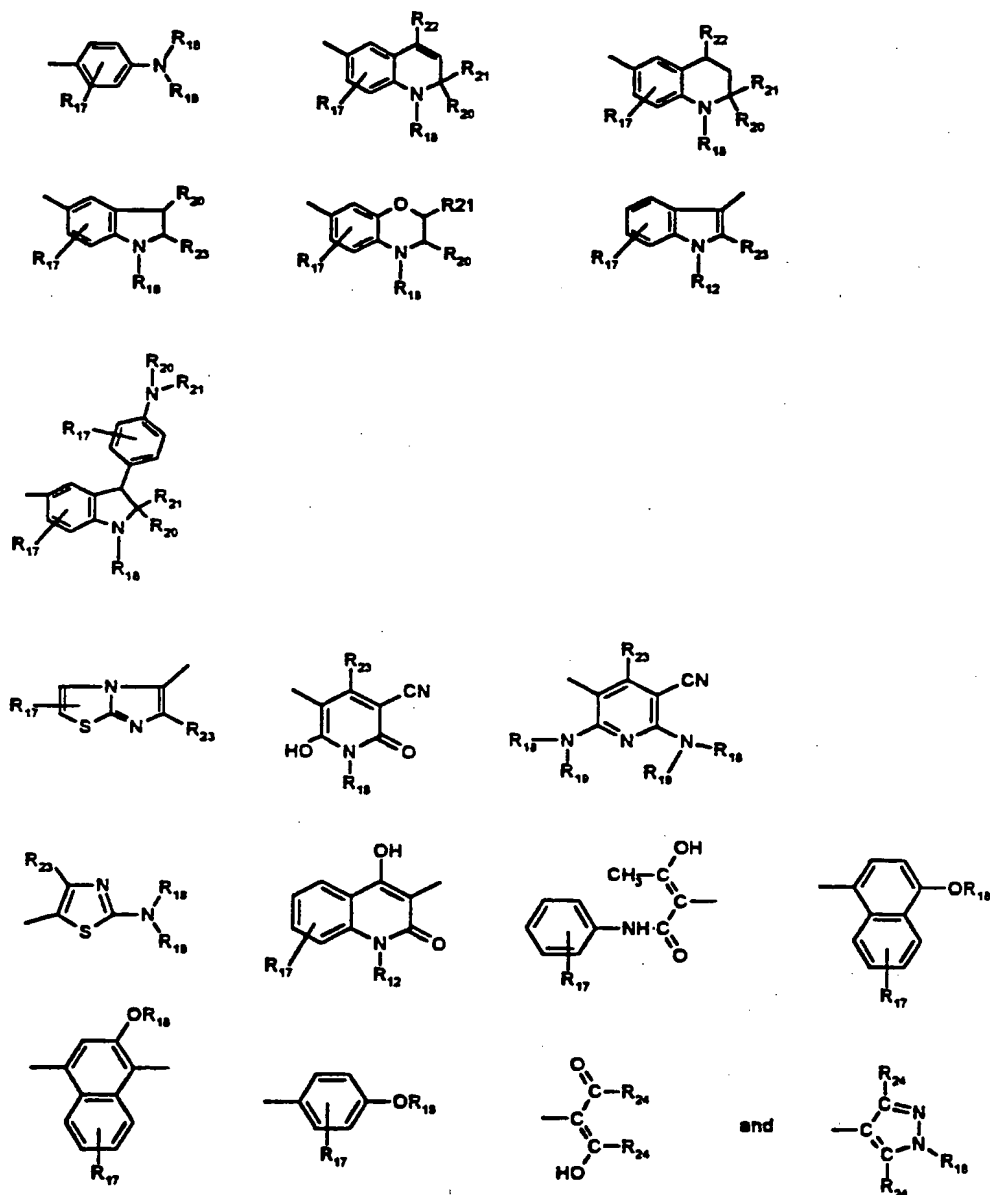
87. The diacidic compounds of claim 71 having the
formula R₆-N=N-Z, wherein R₆ is the residue of a diazotized
aromatic amine and is selected from the group consisting
of

10



wherein Sub₁₂ is one or more groups selected from the group
consisting of hydrogen, C₁-C₆ alkyl, cyano, nitro, C₁-C₆
15 alkylthio, C₁-C₆ alkylsulfonyl, aryl, heteroaryl, arylthio,
arylsulfonyl, halogen, trifluoromethyl, alkanoyl, aroyl,
formyl, NHCO aryl, NHCO C₁-C₆ alkyl, C₁-C₆ alkoxy, carbonyl,
C₁-C₆ alkoxy and - SO₂N (C₁-C₆ alkyl)₂; Q is selected from
the group consisting of -O-, -S-, -SO₂-, -CONH- and -SO₂N
20 (C₁-C₆ alkyl)-; Z is selected from the group consisting of

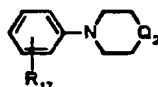
- 232 -



- 5 wherein R₁₇ is selected from the group consisting of hydrogen, 1-2 groups selected from C₁-C₆ alkyl, C₁-C₆

- 233 -

- alkoxy, C₁-C₆ alkylthio, -O- C₂-C₆ alkylene - OH, O-C₂-C₆ alkylene- C₁-C₆ alkanoyloxy, C₁-C₆ alkylene-OH, C₁-C₆ alkylene - C₁-C₆ alkanoyloxy, halogen, C₁-C₆ alkoxycarbonyl, trifluoromethyl, NHCOR₂₄, NHCO₂R₂₄ and
- 5 NHCON(R₂₄) R₂₅, wherein R₂₄ is selected from the group consisting of hydrogen, C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl and aryl; R₂₅ is selected from the group consisting of C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl and aryl; wherein each C₁-C₁₀ alkyl group in R₂₄ and R₂₅ may be further substituted with one or
- 10 more groups selected from the group consisting of C₃-C₈ cycloalkyl, aryl, aryloxy, arylthio, CO₂ C₁-C₆ alkyl, cyano, hydroxy, succinimido and C₁-C₆ alkoxy; R₁₈ and R₁₉ are selected from the group consisting of hydrogen C₁-C₁₀ alkyl, substituted C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl, C₃-C₈
- 15 alkenyl, C₃-C₈ alkynyl, and aryl; R₁₈ and R₁₉ in combination may be combined with another element to which they are attached to form a radical Z having the formula

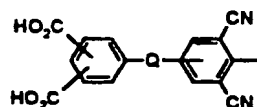


20

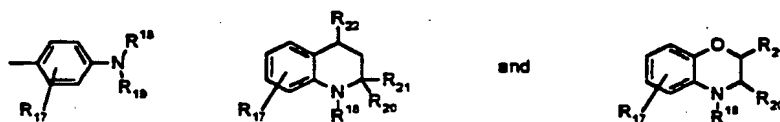
- wherein Q₂ is selected from the group consisting of a covalent bond, -O-, -SO₂-, -S-, -CO-, -CO₂-, -N(COC₁-C₆ alkyl)-, -N(SO₂ C₁-C₆ alkyl)-, -N(CO aryl)-, -N(SO₂ aryl)-;
- 25 R₂₀, R₂₁ and R₂₂ are independently selected from the group consisting of or C₁-C₆ alkyl; R₂₃ is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₃-C₈ cycloalkyl, heteroaryl or aryl; with the provision that no acidic groups be present on Z.

88. The diacidic compounds of claim 87 wherein R₆
- 30 has the structure

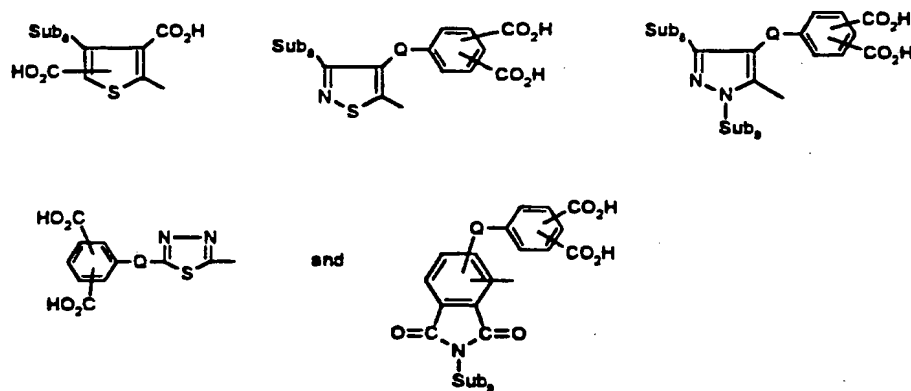
- 234 -



and Z is selected from



89. The diacidic compound of claim 72 wherein R₆ is
residue of a diazotized heterocyclic amine and is selected
5 from the group consisting of

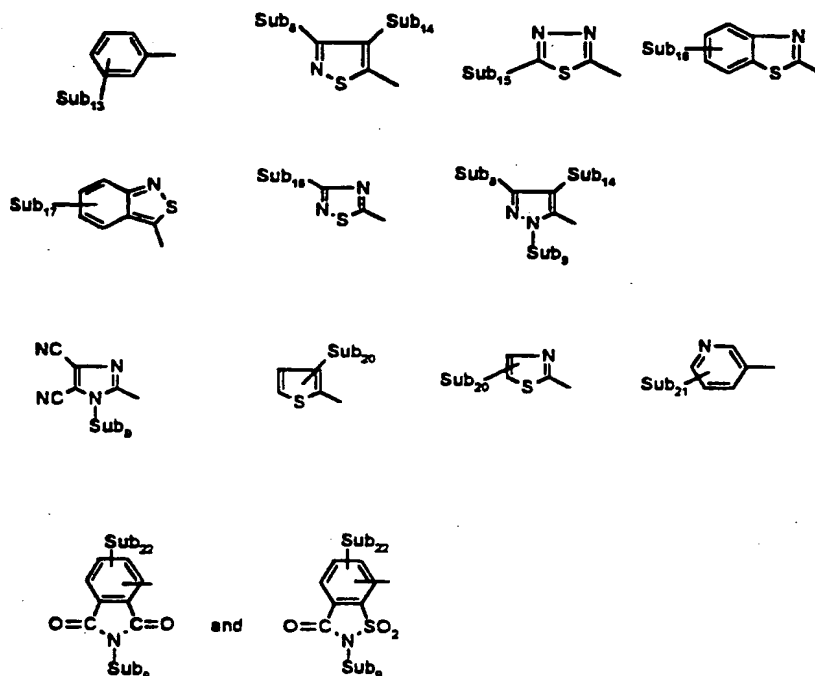


wherein Sub₈ is selected from the group consisting of
10 hydrogen, C₁-C₆ alkyl, halogen, aryl and heteroaryl; Sub₉
is selected from the group consisting of C₁-C₆ alkyl C₃-C₈
cycloalkyl, C₃-C₈ alkenyl, and aryl; Q is selected from
the group consisting of -O-, -S- and -SO₂-; with the
provision that no acidic groups be present on Z.

15

- 235 -

90. The diacidic compounds of claim 72 wherein R_6 is selected from the group consisting of



5

wherein Sub_8 is selected from the group consisting of hydrogen, C_1 - C_6 alkyl, heteroaryl and aryl; Sub_9 is selected from the group consisting of C_1 - C_6 alkyl, C_3 - C_8 cycloalkyl, C_3 - C_8 alkenyl and aryl; Sub_{13} is selected from the group consisting of hydrogen, one or more groups selected from C_1 - C_{10} alkyl, C_1 - C_6 alkoxy, C_3 - C_8 cycloalkyl, halogen, , C_1 - C_6 alkoxycarbonyl, formyl, C_1 - C_6 alkanoyl, C_1 - C_6 alkanoyloxy, dicyanovinyl, C_3 - C_8 -cycloalkanoyl, thiocyno, trifluoroacetyl, cyano, carbamoyl, -CONH C_1 - C_6 alkyl, CONHaryl, $CON(C_1$ - C_6 alkyl) $_2$, $SO_2N(C_1$ - C_6 alkyl) $_2$, CONH C_3 - C_8 cycloalkyl, aryl, aroyl, -N(C_1 - C_6 alkyl) SO_2 C_1 - C_6 alkyl, NHCO C_1 - C_6 alkyl, NHCO C_3 - C_8 cycloalkyl, NHCOaryl, $NHCO_2$ C_1 - C_6 alkyl, $NHCONH$ C_1 - C_6 alkyl, $NHCONH$ aryl, N(C_1 - C_6

10

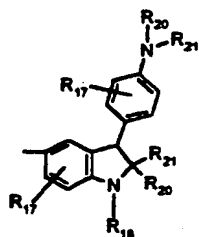
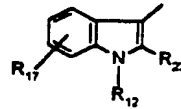
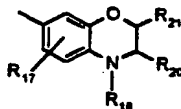
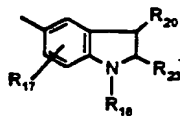
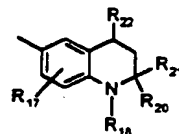
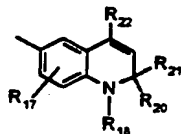
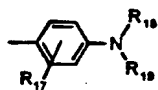
15

- 236 -

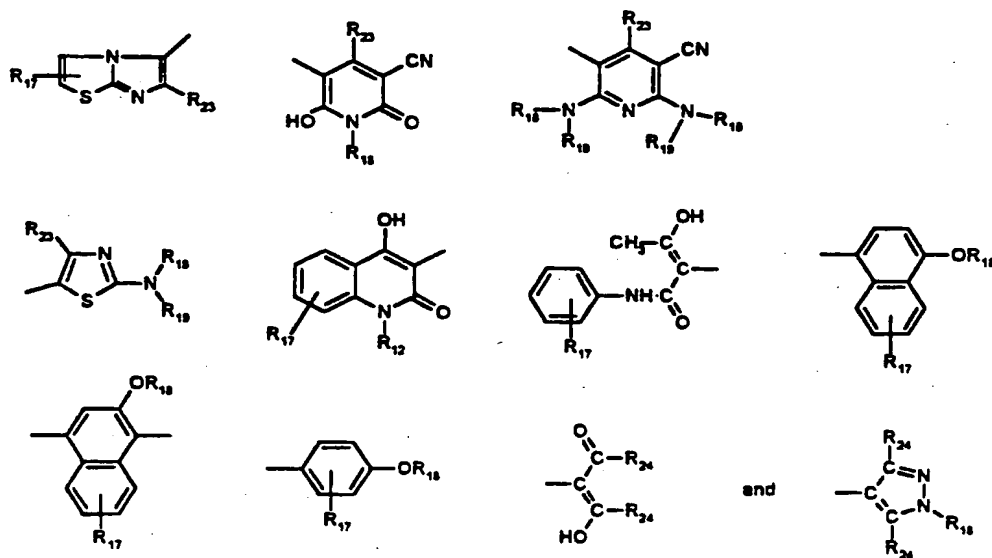
- alkyl)aryl, arylazo, heteroaryl, aryloxy, arylthio, C₃-C₈ cycloalkoxy, heteroarylazo, heteroarylthio, arylsulfonyl, tricyanovinyl, aryloxysulfonyl, C₁-C₆ alkylsulfonyl, trifluoromethyl, fluorosulfonyl, trifluoromethylsulfonyl,
- 5 thiocyano, nitro and CH=D, wherein D is the residue of an active methylene compound selected from the group consisting of malononitrile, α-cyanoacetic acid esters, malonic acid esters, α-cyanoacetic acid amides, α-C₁-C₆ alkylsulfonylacetonitriles, α-arylsulfonylacetonitriles,
- 10 α-C₁-C₆ alkanoylacetonitriles, α-aroylacetonitriles, α-heteroarylacetonitriles, bis(heteroaryl)methanes, 1,3-indanediones, 2-furanones, benzo-2-furanones, naphtho-2-furanones, 2-indolones, 3-cyano-1,6-dihydro-4-methyl-2,6-dioxy (2H)-pyridines, benzo (b) thieno-3-ylidene propane
- 15 dinitrile-5,5-dioxides, 1,3-bis (dicyanomethylene) indanes, barbituric acid, 5-pyrazolones, dimedone, 3-oxo-2,3-dihydro-1-benzothiophene-1,1-dioxides and aryl-C(CH₃)C=C(CN)₂; Sub₁₄ is selected from the group consisting of hydrogen, halogen, cyano, C₁-C₆ alkylthio, arylthio, C₁-C₆ alkoxycarbonyl, nitro, heteroarylthio, C₁-C₆
- 20 alkylsulfonyl, arylsulfonyl, and aryloxy; Sub₁₅ is selected from the group consisting of hydrogen, C₁-C₆ alkythio, C₁-C₆ alkylsulfonyl, aryl, arylazo, -CH=D, cyano, C₁-C₆ alkylsulfonyl, aryl, heteroaryl, arylthio, arylsulfonyl,
- 25 C₁-C₆ alkoxy, trifluoromethyl and C₁-C₆ alkoxycarbonyl; Sub₁₆ is selected from the group consisting of hydrogen, one or two groups selected from halogen, C₁-C₆ alkylsulfonyl, nitro, cyano, C₁-C₆ alkoxycarbonyl, thiocyano and C₁-C₆ alkylthio; Sub₁₇ is selected from the
- 30 group consisting of hydrogen, one or two groups selected from C₁-C₆ alkyl, halogen, nitro and SO₂N (C₁-C₆ alkyl)₂; Sub₁₈ is selected from the group consisting of hydrogen, aryl, C₁-C₆ alkylthio, C₁-C₆ alkylsulfonyl and heteroaryl; Sub₁₉ is selected from the group consisting of hydrogen,
- 35 one or more groups selected from C₁-C₆ alkyl, cyano, nitro, aryl, heteroaryl, arylazo, -CH=D, C₁-C₆ alkoxycarbonyl,

- 237 -

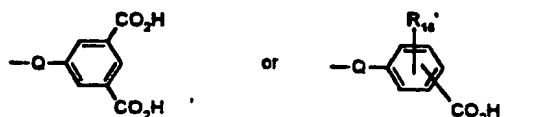
- C_1-C_6 alkylsulfonyl, arylsulfonyl, CONH C_1-C_6 alkyl, C_1-C_6 alkanoyl, aroyl, halogen, formyl and heteroarylazo; Sub₂₀ is selected from the group consisting of hydrogen, one or two groups selected from C_1-C_6 alkyl, aryl, cyano, nitro,
- 5 C_1-C_6 alkoxycarbonyl, C_1-C_6 alkylsulfonyl, arylazo, heteroarylazo, heteroaryl, SO₂N (C_1-C_6 alkyl)₂, formyl, and -CH=D; Sub₂₁ is selected from the group consisting of hydrogen, one to three groups selected from C_1-C_6 alkyl, halogen, cyano, C_1-C_6 alkylthio, C_1-C_6 alkylsulfonyl,
- 10 arylsulfonyl, arylthio, heteroarylthio, C_1-C_6 alkoxy and aryloxy; Sub₂₂ is selected from the group consisting of hydrogen, one to three groups selected from C_1-C_6 alkyl, halogen, C_1-C_6 alkylsulfonyl, nitro, cyano, arylthio and heteroarylthio; Z is selected from the group consisting of
- 15



- 238 -

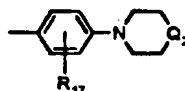


- wherein R_{17} is selected from the group consisting of
- 5 hydrogen, 1-2 groups selected from C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, $-O$ C_2 - C_6 alkylene-OH, O C_2 - C_6 alkylene- C_1 - C_6 alkanoyloxy, C_1 - C_6 alkylene-OH, C_1 - C_6 alkylene- C_1 - C_6 alkanoyloxy, halogen, carboxy, C_1 - C_6 alkoxy, carbonyl, trifluoromethyl, $NHCO_2R_{24}$, $NHCO_2R_{24}$,
 - 10 $NHCON(R_{24})R_{25}$, and $NHSO_2R_{25}$, wherein R_{24} is selected from the group consisting of hydrogen, C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl or aryl, R_{25} is selected from the group consisting of C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl or aryl wherein each C_1 - C_{10} alkyl group in R_{24} and R_{25} may be further substituted with one or
 - 15 more groups selected from the group consisting of C_3 - C_8 cycloalkyl, aryl, aryloxy, arylthio, CO_2H , CO_2 C_1 - C_6 alkyl, cyano, hydroxy, succinimido, C_1 - C_6 alkoxy,



- 239 -

wherein R_5' , R_{16}' and Q are as defined in claim 63; R_{18} and R_{19} are independently selected from the group consisting of hydrogen, unsubstituted C_1 - C_{10} alkyl, substituted C_1 - C_{10} alkyl, C_3 - C_8 cycloalkyl, C_3 - C_8 alkenyl, C_3 - C_8 alkynyl and aryl or R_{18} and R_{19} may be combined with another element to which they are attached to form a radical Z having the formula

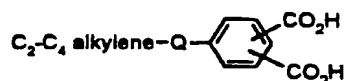
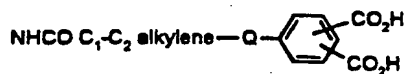


10

wherein Q_2 is selected from the group consisting of a covalent bond, $-O-$, $-S-$, $-SO_2-$, $-CO-$, $-CO_2-$, $-N-(C_1-C_6 \text{ alkyl})-$, $-N(CO \text{ } C_1-C_6 \text{ alkyl})-$, $-N(SO_2 \text{ } C_1-C_6 \text{ alkyl})-$, $-N(CO \text{ aryl})-$, or $-N(SO_2 \text{ aryl})$; R_{20} , R_{21} and R_{22} are independently selected from the group consisting of or C_1 - C_6 alkyl; R_{23} is selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_3 - C_8 cycloalkyl, heteroaryl or aryl; with the provision that two carboxy ($-CO_2H$) groups be on Z , such that the two carboxy groups be present on either R_{17} or R_{18} , or one carboxy may be present on each of R_{17} and R_{18} .

20

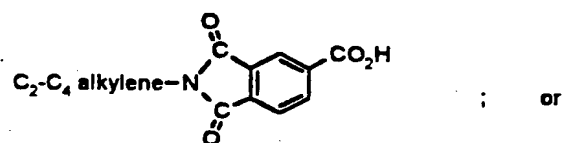
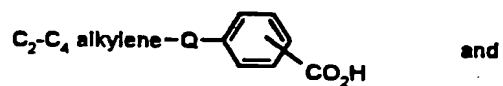
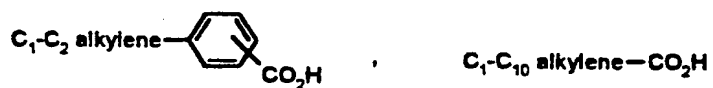
91. The diacidic compounds of claim 90 wherein R_{18} is

25 or R_{17} is

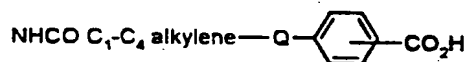
92. The diacidic compounds of claim 89 wherein R_{18} and R_{19} are independently selected from the group consisting of

30

- 240 -



- 5 R_{18} is selected from the group consisting of the groups listed immediately above and R_{17} is selected from the group consisting of



- 10 or $\text{NHCO C}_1\text{-C}_4 \text{ alkylene CO}_2\text{H}$; wherein Q is selected from the group consisting of -S-, -O- or -SO₂-.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/22255

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 6	C09B69/10 C09B29/033 C09B51/00	C08K5/00 C09B29/01 C09B31/02
	C09B1/32 C09B29/08	C09B1/58 C09B29/36 C09B1/62 C09B5/14
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 6 C09B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 778 742 A (ONG BENG S ET AL) 18 October 1988 cited in the application see claims; examples ---	1-92
A	EP 0 040 139 A (EASTMAN KODAK CO) 18 November 1981 see claims; table & US 4 359 570 A cited in the application ---	1-92
A	US 5 030 708 A (KRUTAK JAMES J ET AL) 9 July 1991 see claims; examples ---	1-92
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 24 March 1998		Date of mailing of the international search report 16/04/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Ginoux, C

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/22255

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 417 017 A (EASTMAN KODAK CO) 13 March 1991 see claims; examples 21,31,50 & US 5 032 670 A cited in the application ----	1-92
X	CH 396 833 A (BADISCHE ANILIN- & SODA-FABRIK AG.) 31 January 1966 see compounds 26,27 ----	61
X	FR 2 269 566 A (BAYER AG) 28 November 1975 see claims; example 2 ----	61
X	BE 680 765 A (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 9 November 1966 see example 12 ----	61
X	DE 23 33 828 A (ICI LTD) 17 January 1974 see examples 121,124,130 ----	69-71, 73,85
X	FR 2 229 807 A (ICI LTD) 13 December 1974 see examples 24,25,70 ----	69,72
X	FR 2 243 194 A (SANDOZ SA) 4 April 1975 see example 34 ----	69
X	WO 96 13553 A (ZENECA LTD ;KENYON RONALD WYNFORD (GB); MISTRY PRAHALAD MANIBHAI () 9 May 1996 see examples 2,18,20,31,33,35 ----	72
X	EP 0 356 080 A (ICI PLC) 28 February 1990 see example 2, stage 1, example 8 ----	72
X	JP 08 220 714 A (FUJI PHOTO FILM CO LTD) 30 August 1996 see compounds (D1-9), (D2-4), (ExF-4), (ExF-5) & DATABASE WPI Section Ch, Week 9645 Derwent Publications Ltd., London, GB; Class E19, AN 96-446844 see abstract -----	69,70, 72,78

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. .tional Application No

PCT/US 97/22255

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4778742 A	18-10-88	NONE	
EP 0040139 A	18-11-81	JP 57003851 A US 4359570 A	09-01-82 16-11-82
US 5030708 A	09-07-91	NONE	
EP 0417017 A	13-03-91	US 5032670 A CA 2064802 A,C DE 69007385 D DE 69007385 T EP 0485520 A ES 2062474 T JP 5500078 T WO 9103508 A	16-07-91 01-03-91 21-04-94 13-10-94 20-05-92 16-12-94 14-01-93 21-03-91
CH 396833 A		NONE	
FR 2269566 A	28-11-75	DE 2421375 A GB 1457713 A JP 50151954 A US 3980609 A	04-12-75 08-12-76 06-12-75 14-09-76
BE 680765 A	09-11-66	NONE	
DE 2333828 A	17-01-74	GB 1425029 A AR 197409 A AU 468842 B AU 5698673 A BE 801411 A CA 997754 A CH 575981 A FR 2236900 A JP 49063736 A NL 7309179 A	18-02-76 05-04-74 22-01-76 19-12-74 26-12-73 28-09-76 31-05-76 07-02-75 20-06-74 07-01-74
FR 2229807 A	13-12-74	GB 1448484 A AU 6707374 A AU 6715674 A BE 813109 A	08-09-76 25-09-75 02-10-75 30-09-74

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/22255

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2229807 A		BE 813110 A	30-09-74
		CA 1021504 A	29-11-77
		CH 594103 B	30-12-77
		CH 570774 B	15-02-77
		CH 578085 B	30-07-76
		CH 570874 A	30-01-76
		DE 2419796 A	21-11-74
		DE 2419872 A	07-11-74
		DE 2420134 A	14-11-74
		FR 2227386 A	22-11-74
		FR 2229555 A	13-12-74
		JP 50029890 A	25-03-75
		JP 50029894 A	25-03-75
		JP 50025878 A	18-03-75
		NL 149046 C	
		NL 7405319 A	29-10-74
		NL 7405567 A	29-10-74
		US 3934972 A	27-01-76
		US 3953162 A	27-04-76
		US RE29724 E	08-08-78
FR 2243194 A	04-04-75	CH 584257 A	31-01-77
		AR 206123 A	30-06-76
		AU 7298274 A	11-03-76
		BE 819599 A	05-03-75
		DE 2441524 A	13-03-75
		GB 1471999 A	27-04-77
		JP 50051528 A	08-05-75
		NL 7411613 A	10-03-75
		US 4055556 A	25-10-77
WO 9613553 A	09-05-96	AU 3703595 A	23-05-96
		GB 2306968 A	14-05-97
EP 0356080 A	28-02-90	AT 106930 T	15-06-94
		AU 614413 B	29-08-91
		AU 4020589 A	01-03-90
		DE 68915896 D	14-07-94
		DE 68915896 T	22-09-94
		ES 2055076 T	16-08-94

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/22255

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0356080 A		HK 23297 A	27-02-97
		JP 2140270 A	29-05-90
		US 5053495 A	01-10-91
		US 5203912 A	20-04-93
<hr/>			
JP 08220714 A	30-08-96	NONE	
<hr/>			